

AFAL-TR-88-046

AD:

Final Report
for the period
6 January 1983 to
30 October 1984

Research on High Energy Density Capacitor Materials

April 1988

Author:
R. Somoano

Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109

F04611-83-X-0029

Approved for Public Release

Distribution is unlimited. The AFAL Technical Services Office has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.



Prepared for the: **Air Force
Astronautics
Laboratory**

Air Force Space Technology Center
Space Division, Air Force Systems Command
Edwards Air Force Base,
California 93523-5000

NOTICE

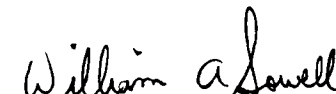
When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any way licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may be related thereto.

FOREWORD

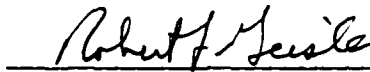
This final report was submitted by Jet Propulsion Laboratory, Pasadena, CA on completion of contract F04611-83-X-0029 with the Air Force Astronautics Laboratory (AFAL), Edwards AFB, CA. AFAL Project Manager was Capt Wayne Schmidt.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.


WAYNE M. SCHMIDT, CAPT, USAF
Project Manager


WILLIAM A. SOWELL, CAPT, USAF
Chief, Advanced Concepts Branch

FOR THE COMMANDER


ROBERT L. GEISLER
Deputy Chief, Astronautical Sciences
Division

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Jet Propulsion Laboratory			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFAL-TR-88-046		
6a. NAME OF PERFORMING ORGANIZATION Jet Propulsion Laboratory		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION Air Force Astronautics Laboratory	
6c. ADDRESS (City, State, and ZIP Code) California Institute of Technology 4800 Oak Grove Drive Pasadena CA 91109			7b. ADDRESS (City, State, and ZIP Code) AFAL/LSVE Edwards AFB CA 93523-5000		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04611-83-X-0029	
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 62302F	PROJECT NO. 3058	TASK NO. 00
			WORK UNIT ACCESSION NO. FV		
11. TITLE (Include Security Classification) RESEARCH ON HIGH ENERGY DENSITY CAPACITOR MATERIALS (U)					
12. PERSONAL AUTHOR(S) Somoano, Robert					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 83/01/06 TO 84/10/30		14. DATE OF REPORT (Year, Month, Day) 88/4	
15. PAGE COUNT 54					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD 20	GROUP 03	SUB-GROUP	Electric Propulsion, Pulsed Plasma Thrusters, Capacitors.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The Pulsed Plasma thruster is the simplest of all electric propulsion devices. It is a pulsed device which stores energy in capacitors for each pulse. The lifetimes and energy densities of these capacitors are critical parameters to the continued use of these thrusters. This report presents the result of a research effort conducted by JPL into the materials used in capacitors and the modes of failure. The dominant failure mechanism was determined to be material breakdown precipitated by heat buildup within the capacitors. The presence of unwanted gas was identified as the source of the heat. An aging phenomena was discovered in polycarbonate based capacitors. CO buildup was noted to increase with the number of times the capacitor had been discharged. Improved quality control was cited as being essential for the improvement of capacitor lifetimes.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL WAYNE M. SCHMIDT, CAPTAIN, USAF			22b. TELEPHONE (Include Area Code) 805-275-5473		22c. OFFICE SYMBOL AFAL/LSVE

TABLE OF CONTENTS

	<u>Page</u>
Introduction	1
Scope of Work	2
Approach	3
Results	7
Analytical Techniques	7
Polysulfone	8
Kapton	9
Mylar	11
Polycarbonate	12
Fluorinerts	12
Capacitor Gas Analysis Results	15
Conclusions	16
References	20
Appendix	39

LIST OF FIGURES

<u>FIGURE</u>	<u>CAPTION</u>	<u>PAGE</u>
1	Schematic of a SNL Capacitor	25
2	Gel Permeation Chromatography	26
3	Gas Chromatography/Mass Spectroscopy	27
4	Fourier Transform Infrared Spectroscopy	28
5	Chemical Structure of Polymers	29
6	Chemical and Thermal Characterisitics of Polysulfone and Polycarbonate	30
7	Isothermal TGA Measurements of Kapton	31
8	FTIR and "Difference" Spectra of Virgin and Pulsed Kapton	32
9	DSC Measurements of Virgin and Pulsed Kapton	33
10	Molecular Weight Distribution of Mylar	34
11	Chemical Structure of Fluoinert Fluids	35
12	GC/MS Data of Fluorinert Model Compounds and SF ₆	36
13	GC/MS Data on Pulsed FC-72	37

LIST OF TABLES

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE</u>
1	PPT Goals and Specifications	21
2	Electrical Properties of Insulators	22
3	Analyses of Capacitor Materials	23
4	Properties of Fluorinert Liquids	24

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special
A-1	



INTRODUCTION

The Pulse Plasma Thruster(PPT) is the simplest and most versatile of electric thrusters. The Air Force Rocket Propulsion Laboratory(AFRPL) has been interested in developing a one millipound solid Teflon PPT for use in North/South spacecraft stationkeeping¹. In this application, the propellant is a solid bar of Teflon which is spring-fed against a retaining shoulder and the thrust chamber. An arc discharge across two electrodes in the chamber ablates the fuel and accelerates it. The device requires two voltages: (a) one for energy storage capacitors; and (b) one for the spark plug ignition system. This report concerns a materials study for the high energy density capacitors.

The goal of the AFRPL program was to obtain a PPT capable of providing ten years of North/South stationkeeping. This requires an ignition/capacitor system capable of 14 million discharges at approximately one discharge every five seconds. The two technical obstacles to achieving this goal were development of the ignition system and the capacitor bank. Considerable progress has been made in the ignition system and the results look encouraging. However, the development of a suitable capacitor bank has been very discouraging. The source of the difficulty is the very high energy density(80J/kg) and long life(14 million discharges) that is required, see Table I². At the necessary voltage levels, 2300V, most capacitor materials degrade severely and lead to failure after only 10^5 shots.

A capacitor is a simple device consisting of two metal electrodes separated by a dielectric medium. Electric energy, stored in the dielectric during charge, can be delivered to a load in a very short time during discharge. The amount of energy stored in the electric field is

$$W=1/2CV^2$$

where C is the capacitance and V is the voltage. On a per unit volume basis, the energy density, E_D is

$$E_D = 1/2 \epsilon_r \epsilon_0 E^2$$

where ϵ_r is the dielectric constant, ϵ_0 is the permittivity of free space, and E is the electric field.

To achieve high energy density materials, one may increase the dielectric constant or the electric field strength. Obviously, there is much to be gained by improving the electric field strength capability because of its nonlinear contribution. In addition, significant increases in the dielectric constant are often accompanied by similar increases in the loss tangent, which leads to excessive heat dissipation and exacerbates material degradation. Most high energy density (HED) capacitors consist of a polymeric dielectric film sandwiched between two metal foil electrodes. This sandwich is rolled into a tight roll and placed into the metal capacitor housing. HED capacitors are impregnated with an organic dielectric fluid to fill any spaces or pockets between the layers and, thus, improve the field stability. Normally, the fluid has a slightly higher dielectric constant than the film and, therefore, the field is concentrated in the film, see Table II. At high electric fields, partial discharges occur in the layers and lead to device failure, especially in repetition rate (rep-rate) applications³. A satisfactory solution to this problem has eluded the capacitor industry and hindered PPT development.

Sandia National Laboratories (SNL) has recently developed a new capacitor technology that seems capable of providing reliable, high energy density devices that should be suitable for PPT application⁴. The keys to this technology are: (a) the use of the unique perfluorocarbon dielectric fluids in multilayer capacitors; and (b) the implementation of stringent controls over material purity and quality, film winding, fluid sparging, capacitor assembly and sealing, and testing. This emphasis on precision, quality control, and cleanliness is reminiscent of procedures adopted by the microelectronics industry, and will likely represent the cornerstone of high energy density capacitor technology in the future. In contrast with conventional capacitor fluids, perfluorocarbons have very low dielectric constants and, thus, the electric field is concentrated in the fluid medium, which has a high breakdown strength, see Table II. Perfluorocarbons are manufactured by 3M under the trademark Fluorinert™. Figure 1 shows a

schematic of a SNL high energy density capacitor. Associated with this new technology are new degradation and failure modes which compromise capacitor performance. Because this technology is so new and has been localized to SNL, little is known of these failure processes.

AFRPL has asked SNL to develop full size perfluorocarbon-based capacitors for PPT evaluation. JPL was invited to collaborate with SNL in order to learn as much as possible about perfluorocarbon-based capacitor materials.

SCOPE OF WORK

JPL was to carry out a materials study with the goals of:

- (a) Determine the physical and chemical characteristics of candidate films and Fluorinert fluids before and after pulse discharge;**
- (b) Identify and recommend appropriate analytical techniques to monitor quality control for improved materials reliability;**
- (c) Identify improved processing steps necessary to remove detrimental impurities; and**
- (d) Determine life limiting chemical degradation processes occurring during pulse operation.**

APPROACH

The first phase of this program involved a literature survey of analytical techniques which would be suitable for this program. From this survey, it was clear that a understanding of the fundamental capacitor material properties was lacking, as well as the correlation of these properties with device performance. Previous work had emphasized macroscopic physical properties, such as the dielectric constant, resistivity, partial discharge, and tensile strength. Fundamental properties are microscopic in nature. Examples are molecular weight, molecular weight distribution, and molecular structure. Changes in this small set of fundamental properties lead to changes in a great number of physical properties. Some examples of this will be given in the next section. It was also clear that this previous reliance on physical properties to characterize capacitor materials was not providing the capacitor engineer with any guidance or insight into the possible materials-related causes of capacitor failure. As a result, an "Edisonian" approach is in place in which, in the event of failure, a new material is pulled off the shelf and substituted for the failed material without any clear understanding of why the previous material failed. In addition, the capacitor engineer could try and "engineer" around the problem. This approach worked well in the past when capacitor requirements did not challenge material limits. However, current and future applications are pushing the extreme limits of available materials, and without a clear understanding of how these materials respond in a high electric field, rep-rate environment, one will not be able to achieve improved performance or suggest approaches for new material development. Thus, particular emphasis was given to identifying and assessing those tools, available at JPL/CIT, which could provide information about the microscopic processes which may be responsible for capacitor material performance.

The second stage of this program involved a baseline characterization. This involved a determination of the fundamental properties of the exact materials(films and fluids) used by SNL in their fabrication of capacitors prior to testing(at Los Alamos), and post-mortem analysis at JPL. SNL chose, and provided, all materials used in this study. Analytical techniques identified from the literature survey were used. Knowing the detailed

characteristics of the virgin(unpulsed) materials greatly facilitated the postmortem analysis of pulsed-to-failure materials.

The postmortem analysis involved use of the same techniques utilized in the baseline characterization. In addition to examining films and fluids to determine nonvolatile reaction products, an insitu Capacitor Gas Analysis Facility was set up to determine gaseous reaction products. These techniques were used not only to provide insight regarding the degradation chemistry, but were also used to assess the efficacy of various capacitor processing techniques.

Capacitor Testing Conditions- Los Alamos(LA) vs AFRPL

A few words should be said about the manner in which the capacitors were pulsed for this program and how it compares to a PPT environment. The following conditions are used at LA: rep rate-1kHz; current reversal-10%(needed to shut off the thyatron switch); discharge time-1 μ s; charge time-400 μ s; duty cycle-1 ms. The AFRPL conditions are: rep rate-0.17 to 1.0 Hz; -30% voltage reversal and -50% current reversal.

In summary, the JPL materials analysis approach clearly reflects the view that the capacitor must be considered as a complex system in which the ultimate performance of the materials depends on their virgin state, how they are handled and processed into capacitors, as well as the capacitor test environment. The key to success is very close interaction with the capacitor engineering activity,i.e., SNL.

RESULTS

The results will be discussed in this section in the chronological order that they were obtained during the program. This should display the connectivity of the work and clarify the thinking behind certain experiments. The first portion will deal with the selection of suitable analytical techniques while the latter portion will deal with the materials study.

Analytical Techniques

Table III shows numerous analytical techniques that are relevant to capacitor material analysis and available at JPL. Clearly, this represents an awesome arsenal with which to study capacitor materials. However, based on the literature and our own in-house experience on the NASA Voyager Spacecraft Polycarbonate Capacitor Failure Program⁵, many of these techniques were judged unsuitable for this particular program. The choice of techniques reflects the actual materials to be studied, the desired sensitivity, our emphasis on obtaining information of a fundamental nature, and the scope of the program. As examples, molecular weight(MW), molecular weight distribution(MWD), chemical structure, degree of crystallinity, and crystallization and glass transition temperatures represent fundamental information that we were interested in and felt could be obtained within the scope of the program. Consequently, GPC, FTIR, GC/MS, DTA, TGA, and DSC were selected as the techniques for use in this program. The names and corresponding abbreviations of the techniques are given in Table III. It is unfortunate that one must deal with such an "alphabet soup", but it greatly simplifies discussion. It should be noted that NMR also provides fundamental information, especially for crystalline materials such as polypropylene. Since this was not a candidate material and NMR can be a somewhat involved measurement, this technique was not pursued. Mechanical measurements were deemed not sensitive enough to be used at this stage.

Figures 2,3, and 4 show examples of GPC, GC/MS, and FTIR equipment and analysis, respectively. GPC, and also High Pressure Liquid Chromatography(HPLC), are used to determine MW and MWD changes in the dielectric films. The example in the figure shows a shift and

broadening in these two parameters as a result of thermally aging polyethylene vinyl acetate. This can compromise mechanical properties and induce brittling and subsequent failure. Similarly, impurities and additives such as UV stabilizers and antioxidants (which may not be necessary for capacitor applications), can also be detected. GC/MS provides an analysis of the impregnating fluid as well as of gaseous impurities and reaction products. We have adapted our Electronic Package-Chemical Analysis facility such that SNL capacitors can be punctured insitu and the escaping gases analyzed. Figure 4 shows an example of the gas analysis of a polycarbonate capacitor before and after discharge in which oxygen and CO are found to increase. Since the insitu Capacitor Gas Analysis Facility is a new and unique capability in this field, a more detailed description, together with drawings and sample data, is included as an Appendix to this report. FTIR can be used to examine both film and fluid to obtain information regarding chemical bonds. In particular, the ability to digitize the spectrum allows one to subtract what appears to be identical spectra of materials before and after abuse to obtain the difference spectrum in which very subtle changes are readily seen. An example of this is shown in Figure 4 for the benzene/toluene solution. It should be noted that the techniques chosen for this study are, in many cases, complementary. Thus, chemical reactions suggested by DSC measurements can be verified by FTIR studies.

The film materials which were studied for this program were polysulfone(PS), Kapton, Mylar, and polycarbonate(PC). The impregnant fluids were the perfluorocarbons(Fluorinert-72 and its derivatives). The common thread behind the choice of these materials is the belief that thermally induced chemical degradation is a key failure mode of perfluorocarbon-based capacitors. Thus, materials with high thermal stability were sought. While Mylar is not very thermally stable, it was briefly studied as a test of this hypothesis. The structures of these materials are shown in Figure 5. Table IV lists the properties of some Fluorinert fluids.

Polysulfone

Polysulfone and polycarbonate were the first materials studied since their high glass transition temperatures, T_g , dielectric constants, and

breakdown strengths made them ideal candidates for PPT use. Howard Mauldin (SNL) had initially investigated polypropylene/Fluorinert capacitors and had achieved pulse lives -10^6 at 3.5 kV/mil^4 . However, with polysulfone similar performance was achieved at fields of -4.7 kV/mil , reflecting a much higher energy density (by a factor of $(4.7/3.5)^2$)⁴. There was also a variation in polysulfone capacitor performance. Therefore, our first study of this material, as well as polycarbonate, involved thermal (DTA) measurements to determine T_g , and HPLC to monitor MW and MWD. The results are shown in Figure 6. The first point to notice is that the polysulfone is not pure, but contains polycarbonate at a significant level. The T_g 's of pure PS and PC are 190°C and 158°C , respectively. The DSC data show two changes of slope, corresponding to two T_g 's at 167°C and 138°C . This indicates that the T_g 's of PS and PC have each been lowered and that they are mixed together in a blend formation as opposed to a block formation. A decrease in T_g can be very serious since above T_g a material becomes rubbery and compromises mechanical integrity and capacitor structure. Since T_g varies as molecular weight, HPLC measurements were carried out. As seen in Figure 6, an -12% decrease in molecular weight is noted (large elution volumes correspond to small molecular weights). Since the MWD was not broadened, this indicates a degradation involving chain zipping in which the polymer chains are fragmenting from the ends. Evidently, the molecular weights of these particular films were high enough such that the small changes did not result in any serious decline in T_g in the pure materials. The conclusions are that chemical degradation is occurring and that quality control of materials must be stressed. Simple and routine thermal measurements, such as DSC, can be most valuable in this respect. At this point in the program, it was discovered that polysulfone was becoming very scarce and would only be available in very limited thicknesses. Thus, it was decided to put PS "on the back burner" and concentrate our attention on Kapton.

Kapton

Kapton is an amorphous, crosslinked polyaromatic imide manufactured by DuPont. Its crosslinked structure imparts a high degree of thermal

stability (decomposition temperature $>400^{\circ}\text{C}$), but T_g is no longer meaningful. Since it is not crystalline, a melting temperature, T_m , is also not relevant. SNL had obtained promising performance using Kapton/PC-72 capacitors. By heat sinking these capacitors at 50°C to 60°C , pulse lifes of the order of 10^6 had been obtained at fields of 4.5 kV/mil and at 1 kHz. However, the Kapton film was very sticky and difficult to wind. This was believed to be due to residual high temperature solvents which remained in the film. Attempts by SNL to outgas the film at 50°C was ineffective in that the material continued to outgas for long periods of time. At this point, JPL initiated an effort to identify the impurities and to develop improved outgassing procedures. After reviewing the extensive Kapton data at JPL, we carried out a series of GC/MS measurements of Kapton to identify the gases coming out at 75°C . We found H_2O , CO_2 , amines, and amides to be the principal gaseous impurities. Based on these results, we performed thermal experiments to identify the relative amount of impurities. We found that - 1-2% of impurities were present. We then carried out a series of isothermal TGA experiments in which a specific film temperature is chosen and held constant while the mass of the film is monitored as a function of time. In this way, one can find an optimum temperature at which the film does not degrade, yet the impurities are removed in a reasonable time. Figure 7 shows typical results. The top figure corresponds to a constant temperature of 50°C as used at SNL. Even after one hour, the film weight has not stabilized. In contrast, the bottom figure, corresponding to 120°C , shows that the film has been completely outgassed in 10 minutes. This information was passed on to SNL for incorporation into their capacitor processing and represents an excellent example of how materials studies can directly benefit engineering activities on a short time scale.

At this time, we received three samples of Kapton film that had been pulsed-to-failure at 4.5 kV/mil at 1.1 kHz. These films had exhibited lifes of: (a) 8.8×10^5 at 57°C ; (b) 1.8×10^6 at 48.2°C ; and (c) 2.6×10^6 at 48.5°C . Because of the crosslinked structure of Kapton, it has practically no solubility and, therefore, is unsuitable for GPC or HPLC studies. Therefore, we carried out FTIR studies to examine the stability of the chemical bonds under prolonged pulsing. Figure 8 shows the results of this study. The top two figures show the raw spectra and the arrows indicate areas where we

think changes have occurred. Note that these raw spectra correspond to the traditional infrared spectra and are not sensitive to small changes. These two spectra have been digitized and subtracted. The "difference" spectra are shown at the bottom of the figure. We have only shown certain wavenumber (or wavelength) regions where the changes occurred. The key features can be seen in reference to the chemical structure formula shown below the figures. The main thing to notice is that the polyimide has undergone hydrolysis (i.e., reacted with water) to form a polyacid amide. In particular, the H_2O has attacked the carbon-nitrogen bond, resulting in ring cleavage. This gives rise to a carboxylic acid pendant group and produces an amide linkage in the backbone. These results support the GC/MS findings. Although this degradation has occurred, it appears to be in fairly low concentration. We have also carried out thermal measurements on these samples in order to corroborate the optical studies. Figure 9 shows the results of a DSC scan of the pulsed films. The point to note is the "bump" at 320°C. This bump corresponds to the normal isomerization reaction involving the imide group. If this bond has been disrupted via degradation mechanisms, less of it will be around for the isomerization reaction. This is exactly what is observed, i.e., the size of the bump diminishes with pulse life. Note that temperature seems to be more detrimental than pulse life. In summary, the DSC, FTIR, and GC/MS measurements all confirm that a small degree of chemical degradation is occurring upon pulsing. The impurity, H_2O , is likely very active in this degradation and, thus, efforts to remove water via the suggested outgassing procedure at 120°C is worthwhile.

Mylar

At this point, it was decided to carry out a short study of Mylar in order to further test the theory of thermal-induced chemical degradation. SNL had tested some Mylar/Fluorinert capacitors and had found that the breakdown strength of pulsed-to-failure film had degraded considerably. Since Mylar has a very low T_g , we decided to see if the molecular weight of the material had undergone any change. Mylar is partly crystalline and, thus, has limited solubility. Therefore, HPLC studies had to be performed at high temperature. Three pulsed-to-failure films plus one virgin unpulsed sample were examined. The three films had undergone 260, 5820, and 14000 discharges. All films had a dominant molecular weight

peak centered around 10^6 . The 260 and 14000 shot films appeared similar to the virgin film. However, the 5820 shot film clearly showed a new low molecular weight peak centered at -2000, see Figure 10. Thermal measurements indicated no anomalous behavior among the T_g 's for all three films. Thus, the slight change in the molecular weight of the 5820 shot film did not appear to be associated with any significant structural or thermal change. We later learned that the 5820 Mylar film may have been subjected to excessive winding at SNL's GE plant. In summary, the results on Mylar have not led to clear conclusions. Since this was not a candidate film for the PPT program, further work on Mylar was discontinued. However, it does seem that Mylar would be a useful material to study in order to understand generic failure modes in dielectric films.

Polycarbonate

Some preliminary measurements have also been made on polycarbonate (PC). This material appears to be the most promising for PPT applications because of its high T_g (165°C), its ability to support high electric fields for long pulse life, and its availability in many thicknesses⁴. This latter point is quite important since it allows one to select the optimum thickness for use in a multilayer configuration while maintaining the same dielectric thickness. A multilayer capacitor should be beneficial since it should provide enhanced evaporative cooling. Chemical and thermal measurements on PC did not indicate the presence of moisture as found in Kapton, and no changes were observed in the glass or melting temperatures in pulsed-to-failure films. Thus, capacitor failure did not lead to large changes in the PC film. More sensitive measurements should be done.

Fluorinert/SF₆

Having carried out studies of several film materials, we now turned our attention to the Fluorinert fluids and its additive, SF₆. The fluid is one of the key components since, as mentioned earlier, it carries most of the field stress in perfluorocarbon-based capacitors. Equally important, it is believed that the success of the perfluorocarbon technology rest on the cooling capability of these fluids. Note that the boiling point of these fluids

varies with the molecular weight, see Table IV. One desires a low boiling point fluid since it provides better evaporative cooling. However, if the boiling point is too low the fluid will be in the vapor state most of the time and not provide the desired cooling. Thus, one needs to optimize the fluid constituency. In order to achieve high field stability, it is critical that the fluid be completely outgassed, or "sparged", of gaseous impurities. Normally this is done by bubbling an benign gas through the fluid prior to filling the capacitor. In recent years, SF_6 has been used as this gas. SF_6 is an electronegative gas with a high breakdown strength, see Table II. It is also believed to act as a scavenger of unwanted impurities and degradation products. This hypothesis has not been confirmed. It is clear that the sparging process is very important and amenable to optimization.

During the course of this program, several important observations were made at SNL and Los Alamos (by Clark Thompson): (a) the first version of the sparging process involved uncontrolled, and unoptimized, flow of SF_6 through the Fluorinert; (b) the second version, intended to improve control of the SF_6 flow rate, led to inadvertent exposure of the fluid to atmosphere, thereby, providing a possible opportunity for the escape of SF_6 and inclusion of gaseous impurities; (c) during the pulse discharge and thermal modeling study at Los Alamos, it was discovered that the heat dissipated in the capacitors exceeded that predicted to be associated with the equivalent series resistance (ESR). It was hypothesized that the extra heat was associated with excessive gaseous products or impurities in the capacitors; and (d) an interesting peak in the noise spectrum was observed at Los Alamos and believed to be associated with the presence of SF_6 ⁴. If this were true, the noise spectrum could serve as a useful nondestructive, insitu indicator of the additive. However, the peak was observed in some capacitors but not in others. As a result of these observations, it became clear that we did not know how much SF_6 was actually going into the fluid or whether SF_6 was even the beneficial agent it was assumed to be. In addition, we did not know the nature of the gaseous impurities in the capacitors. For example, argon was sometimes used to purge the film of trapped air prior to evacuation and filling with Fluorinert. If this purging and outgassing were incomplete, the residual gases could serve as sources of heat generation. This could also lead to degradation of the Fluorinert fluid. Thus, JPL turned its attention to the study of fluid degradation and

the identification of gaseous species. The fluids which were examined were those associated with the Kapton and Mylar samples described above.

The first phase of the Fluorinert studies was to carry out the baseline characterization. GC/MS was selected as the technique to use. Figure 11 shows the chemical structure of perfluorocarbons. An important point to note is that significant degradation will likely involve changes in the value of x and, hence, the molecular weight should change in a discrete manner rather than continuously. High molecular weight molecules could degrade into smaller fragments and, similarly, smaller molecules could combine to form larger molecules. Thus, the boiling point and the evaporative cooling capability will likely be compromised by fluid degradation. Figure 12 shows the baseline GC/MS data for: (a) unpulsed FC-72 (the fluid most used in the SNL capacitors); (b) a low molecular weight fluid, FC-87, with a boiling point, b.p., of $<56^{\circ}\text{C}$; (c) a high molecular weight fluid, FC-77, b.p. $=97^{\circ}\text{C}$; and (d) pure SF_6 . The vertical axes are arbitrary units of intensity, roughly proportional to species concentration, while the horizontal axes are directly proportional to molecular weight. Our goal was to identify the specific scan numbers associated with each of these model compounds in order that they could be used in the analysis of pulsed fluids.

Twenty-five pulsed samples were examined, including "blind controls" provided by SNL. Figure 13 shows typical data. The key points to notice are: (a) a low molecular weight (hence, volatile) species originally present in the unpulsed fluid is removed during the sparging process. This was not always the case, indicating variable outgassing procedures; (b) SF_6 is present. However, by comparing the ratios of peak heights within a given spectrum, it was clear that the amount of SF_6 varied considerably; (c) there is a growth ($\sim 5\%$) of a high molecular weight component in the fluid upon pulsing. It appears likely that the fluid is degrading to yield low molecular weight fragments which combine to form high molecular weight molecules. This obviously could lead to an increase in the b.p., thereby reducing evaporative cooling and exacerbating thermal problems; and (d) the growth of the high molecular weight component scales inversely with the concentration of SF_6 . Low SF_6 concentrations were associated with large buildups of high molecular weight components. Thus, SF_6 may indeed have a beneficial effect; and (e) there appears to be more of the high molecular weight components in Mylar capacitors than in those with

Kapton. It should be noted that this is the first time such measurements have been made for the purpose of capacitor use. The immediate result of these measurements was that SNL designed an improved sparging process to better control SF_6 concentration.

Capacitor Gas Analysis

The final phase of this program dealt with the development of an insitu Capacitor Gas Analysis Facility in which hermetically sealed, pulsed capacitors from SNL could be placed, and punctured, under vacuum in order to analyze the gas composition. This represents a unique capability in the capacitor field. As mentioned earlier, a detailed description, with photos, is given in Appendix I. Three-, four-, and five-layer polycarbonate/FC-72 pulsed capacitors were examined. Typical data are shown in Appendix I. The results showed the N_2 , Ar, CO, and O_2 were present. However, it was the distribution of these species among the capacitors that was more interesting: (a) the capacitors with the highest pulse life (the four-layer capacitors- 10^8 shots at 1.1kHz/4.0 kV/mil) exhibited the most CO. This indicates for the first time a "wear-out" or aging process in which prolonged pulsed discharge leads to gradual polymer chain degradation. Note that it is not clear that this is the cause of capacitor failure. Perhaps, with even longer pulse life this would be a failure mode; (b) Argon was found in capacitors which inadvertently had not been purged completely. More exciting, these same capacitors were found to have the lowest life and the highest heat generation. Thus, for the first time, heat buildup, low life, and gaseous impurities have been tied together. Only a combined electrical, chemical, and capacitor fabrication effort could have made this correlation possible.

CONCLUSIONS

This program has demonstrated that combining materials studies with capacitor engineering activities can lead to improvements in quality of materials and process controls, and provide valuable insight into capacitor material degradation and failure modes. Numerous analytical techniques were identified which would be useful for capacitor material analysis. Of these, GPC, HPLC, GC/MS, FTIR, DTA, TGA, and DSC were selected and found to be simple and effective. This combination of chemical, optical, and thermal techniques provided complementary information and, thus, incorporates a series of checks and balances in the interpretation of results. A thorough baseline characterization was performed on all materials that were used in the SNL capacitors. The materials then underwent postmortem analysis after pulsed-to-failure using the same techniques.

Polysulfone, polycarbonate, Mylar, and Kapton films were investigated. A modest amount of work was spent on PS since its scarcity and very limited thicknesses preclude it from extensive near-term use. It does appear to be a promising material when it can be obtained pure. DSC measurements were shown to be a convenient way to routinely assess the quality of this material. Mylar was investigated in order to gain more understanding of thermally-induced chemical degradation. The molecular weight of the material was found to degrade into a bimodal distribution with excessive winding. The influence of the pulse discharge environment on the material properties were not clearly established. Kapton received considerable attention due to its high thermal stability. Water, carbon dioxide, amines, and amides were found in ~1-2% concentration. Their presence led to difficulties with sticking and winding. Thermal studies were used to develop an improved outgassing procedure, which was recommended to SNL. Specific degradation in the Kapton ring structure was identified, although it was not extensive. Polycarbonate appears to be the most promising material, both in terms of material stability as well as in capacitor tests.

The Fluorinert fluids were examined by GC/MS. Model compounds were used in the baseline characterization. Test results of pulsed fluids

showed that they suffered slight decomposition in which the low molecular weight decomposition fragments combined to yield large molecular weight products. The degree of fluid decomposition was found to scale inversely with the concentration of the additive, SF_6 . The concentration of SF_6 , as well as low molecular weight impurities, was found to vary in the fluids, indicating variations in the outgassing and sparging process.

Finally, a unique Capacitor Gas Analysis Facility was developed to carry out insitu studies of the capacitor gas composition. The results revealed the first evidence of a wear out, or aging, process in which the concentration of CO was found to scale with pulse life in PC capacitors. In addition, some capacitors were found to have excessive argon present. This gas is a residue of incomplete outgassing of the film. Capacitors with excessive argon had the shortest life and the largest heat buildup. These results are extremely important since they tied excessive gaseous species with excessive heat and short life. Such measurements should definitely be pursued in the future.

SUMMARY- FAILURE MECHANISMS

Excessive heat buildup associated with the presence of unwanted gases is a major failure mechanism in high energy density capacitors. It results in shorter capacitor life, ostensibly via materials degradation. These gases, e.g., argon and air, occur because of: a) incomplete outgassing of the film and fluid; b) incomplete removal of the capacitor purging gas; c) incomplete sparging of the fluid; and d) the generation of gaseous degradation products. The presence of SF_6 (as a deliberately added product, i.e., an additive) seems to mitigate the deleterious thermal effects of extraneous gases. The removal of these gases, as well as the addition of SF_6 , to the required level of confidence is difficult, challenging, and merits further work. Similarly, this program has provided the first evidence of an "aging", or "wear-out" mechanism associated with long pulse life, i.e., the gradual unzipping of polycarbonate to yield CO products, and the degradation of the perfluorocarbon fluid to yield high molecular weight gaseous species. As mentioned above, both of these mechanisms yield gaseous products which can contribute to thermal buildup. The distinction between degradation modes and failure mechanisms must be kept in mind. For example, it is not clear that the modest degradation of the FC-72 fluid

or the generation of CO lead to capacitor failure. At this time, the presence of extraneous gases appears to be a more serious problem. These conclusions are new and preliminary in nature. More work must be done in this area.

SUMMARY- PROCESSING TECHNIQUES

This program has clearly shown the difficulties which the capacitor engineer encounters in handling the gas impurity problem. We recommend: a) the use of DTA measurements to establish the optimum, and safe, conditions for outgassing films; b) extensive vacuum pumping to insure removal of purging gases; c) improvements in sparging to insure the saturation of the fluid with SF_6 , e.g., atomizing the gas via frits and increasing the liquid pathlength through which the SF_6 passes; and d) insitu GC/MS measurements of capacitors, coupled with thermal studies similar to those carried out at Los Alamos, to monitor gas composition and concentration, and associated heat buildup.

A few words should be said regarding materials degradation for capacitors tested at LA versus AFRPL. As mentioned on p. 6, the higher rep rate used at LA should be a more severe test since there is more heat dissipated, e.g., 500W vs. 200W at AFRPL. However, the greater degree of voltage/current reversal at AFRPL may alter this situation. This reversal suggest an underdamped system in which the load and the capacitor resistance are not optimally matched. This will lead to a greater dissipation of heat in the capacitor, compromising materials stability. Similarly, the spikes observed on the AFRPL voltage and current waveforms may lead to excessive charge oscillation and commensurate degradation processes. This is a very important point. It should be determined whether these spikes, possibly associated with noisy switches(??) will always be present, or whether the system can be redesigned to eliminate them. If they cannot be eliminated, their impact on materials stability and capacitor performance must be determined.

This work clearly shows the importance of quality control for materials and processing. Few capacitor engineering activities have attempted to verify the nature of the materials they use or confirm what they think they are putting into the capacitor. This work demonstrates that even with

modest care, there can be considerable variations in capacitor composition which can profoundly influence capacitor performance. Only by optimizing each step in the capacitor manufacturing process, and appreciating the system(i.e., interactive) nature of the problems, can one hope to achieve future requirements. The correlation of materials analysis data with capacitor performance is still in the infant stage, but with more work and close interaction with the capacitor engineer, such efforts should bear considerable fruit, especially for future technologies where extreme performance is required.

REFERENCES

1. Vondra, R.J., AIAA/ISASS/DGLR 16th International Electric Propulsion Conference, New Orleans, LA. (1982).
2. Galperin, I., Final Technical Report, Maxwell Report No. MLR 1807, Sept., 1984.
3. Sarjeant, W.J., Rohwein, G.J., Mauldin, G.H., Bickford, K.J., Springer, T.E., and Burkes, T.R., Appl. Phys. Commun., 3, 83 (1983).
4. Mauldin, G.H., Proc. NAS/IEEE Symposium on High Energy Density Capacitors and Dielectric Materials, Boston, MA (1980); Proc. NAS/IEEE Symposium, Huntsville, AL (1981); Proc. of the CEIDP Conf., Claymont, DE (to be published).
5. Ott, F., Yen, S.P.S., and Somoano, R.B., Special Issue of the IEEE Transactions of Electrical Insulation (to be published).

TABLE 1. PPT GOALS AND SPECIFICATIONS

SPECIFICATION	GOALS
ENERGY	190 J AT 2.2 kV
VOLTAGE	2.2 kV $\pm 1\%$
VOLTAGE REVERSAL	25%
CAPACITANCE	80 μ F + 10% - 5%
INDUCTANCE	15 nH
LOSS FACTOR	0.010 GOAL 0.013 (MAXIMUM AT 25°C, 120 Hz)
PEAK CURRENT	30 kA
INITIAL di/dt	10 ¹⁰ A sec ⁻¹
PULSE RATE	0.17 Hz (NORMAL) 1.00 Hz (MAXIMUM)
BURST DURATION	INDEFINITE
CAPACITOR TEMPERATURE	-20°C TO +50°C (DESIGN)
RANGE	-35°C TO +70°C (GOAL)
AMBIENT PRESSURE	10 ⁻⁴ Torr
RADIATION ENVIRONMENT	UNSPECIFIED INTENSITY
LIFE	10 ⁷ SHOTS
RELIABILITY	NOT SPECIFIED
GROSS ENERGY DENSITY	88 J/kg (40 J/lb) @ 2.2 kV
WEIGHT	4.75 lbs
SHAPE	CYLINDRICAL
DIMENSIONS	10.5 cm (4.125 in.) OD, 18.4 cm (7.25 in.) LENGTH

TABLE 2. ELECTRICAL PROPERTIES OF INSULATORS

	κ	V_b V/mil
AIR	1.000585	75
ALUMINUM OXIDE	7.0	300
BAKELITE (GENERAL PURPOSE)	6.0	300
CASTOR OIL	3.7	350
CERAMICS	5.5-7.5	200-350
ETHYLENE GLYCOL	39	500
HIGH-VOLTAGE CERAMIC (BARIUM TITANATE COMPOSITE AND FILLER)	500-6000	50
KAPTON (POLYAMIDE)	3.6	7000
KRAFT PAPER (IMPREGNATED)	6	2000
LUCITE	3.3	500
MYLAR	2.5	5000
PARAFFIN	2.25	250
POLYCARBONATE	2.7	7000
POLYETHYLENE	2.2	4500
POLYPROPYLENE	2.5	9600
POLYSTYRENE	2.5	500
POLYSULFONE	3.1	8000
PYREX GLASS	4-6	500
QUARTZ, FUSED	3.85	500
RECONSTITUTED MICA	7-8	1600
SILICONE OIL	2.8	350
SULFUR HEXAFLUORIDE	1.0	200 (PER ATM)
SULFUR	4.0	--
TANTALUM OXIDE	11.0	100
TEFLON	2.0	1500
TITANIUM DIOXIDE CERAMICS	15-500	--
TRANSFORMER OIL	2.2	250-1000
WATER	80	500

(PULSE CHARGED IN
7 TO 10 μ S)

TABLE 3.

ANALYSES OF CAPACITOR MATERIALS

GENERIC NATURE OF THE TESTS	DESIRED INFORMATION	ACTUAL TEST
<u>CHEMICAL</u>	<ul style="list-style-type: none"> • MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION • CHEMICAL STRUCTURE • WETTABILITY • NATURE OF IMPURITIES AND ADDITIVES 	<ul style="list-style-type: none"> • GEL PERMEATION CHROMATOGRAPHY (GPC) • FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) • CONTACT ANGLE • GAS CHROMATOGRAPHY/MASS SPECTROSCOPY (GC/MS) • ELEMENTAL ANALYSIS • EMISSION SPECTROSCOPY • ENERGY DISPERSIVE SPECTROSCOPY (EDS) • ION MICROPROBE
<u>STRUCTURAL</u>	<ul style="list-style-type: none"> • DEGREE OF CRYSTALLINITY AND ORIENTATION • SURFACE MORPHOLOGY 	<ul style="list-style-type: none"> • X-RAY DIFFRACTION • SMALL ANGLE X-RAY SCATTERING (SAXS) • SCANNING (TRANSMISSION) ELECTRON MICROSCOPY (SEM/TEM) • OPTICAL MICROSCOPY • NUCLEAR MAGNETIC RESONANCE (NMR)
<u>MECHANICAL</u>	<ul style="list-style-type: none"> • DENSITY • TENSILE STRENGTH • TEAR STRENGTH • ELONGATION • CRYSTALLIZATION TEMPERATURE 	<ul style="list-style-type: none"> • DENSITY • STRESS-STRAIN • TEAR TEST
<u>THERMAL</u>	<ul style="list-style-type: none"> • THERMAL AND OXIDATIVE STABILITY LIMITS 	<ul style="list-style-type: none"> • DIFFERENTIAL THERMAL ANALYSIS (DTA) • DIFFERENTIAL SCANNING CALORIMETRY (DSC)
<u>ELECTRICAL</u>	<ul style="list-style-type: none"> • ELECTRICAL LOSSES, LEAKAGE 	<ul style="list-style-type: none"> • THERMAL GRAVIMETRIC ANALYSIS (TGA) • DIELECTRIC CONSTANT • TAN δ • IMPEDANCE

TABLE 4. PROPERTIES OF FLUORINERT LIQUIDS

PROPERTY	FC-72	FC-77	FC-104	FC-75	FC-40	FC-43	FC-70	WATER [■]
TYPICAL								
BOILING POINT, °C	56	97	101	102	155	174	215	100
POUR POINT, °C	-90	-110	-65	-88	-57	-50	-25	0
AVERAGE MOLECULAR WEIGHT	340	415	435	420	650	670	820	18
SURFACE TENSION dynes/cm	12	15	14	15	16	16	18	72
CRITICAL TEMPERATURE, °C	178	251*	230*	227	277	303*	337*	374
CRITICAL PRESSURE, ATMOSPHERE	18.1	14.8*	15.5*	15.8	14.6*	14.1*	6.7*	218
REFRACTIVE INDEX (n _D)	1.251	1.280	1.271	1.276	1.290	1.291	1.303	1.333
ACOUSTIC VELOCITY meters/sec	512	595	575	585	640	655	687	1498
VAPOR PRESSURE, torr	232	42	29	31	3	1	<0.1	23
SOLUBILITY OF WATER ppm	10	13	11	11	7	7	8	Complete
SOLUBILITY OF AIR ml./100 ml.	48	50	38	40	27	26	22	1.9
DENSITY, g/ml.	1.68	1.78	1.76	1.76	1.86	1.85	1.94	1.0
VISCOSITY, centistokes	0.4	0.8	0.8	0.8	2.4	2.6	13.4	0.9
SPECIFIC HEAT, cal./g) (°C)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.0
HEAT OF VAPORIZATION AT B.P. cal/g	21	20	22	21	17	17	16	540
THERMAL CONDUCTIVITY milliwatts/(cm ²) (°C/cm)	0.57*	0.64	0.64*	0.64	0.66*	0.67	0.71*	5.86
COEFFICIENT OF EXPANSION ml./ml.) (°C)	0.0016	0.0014	0.0014	0.0014	0.0012	0.0012	0.0010	0.0002
VOLUME RESISTIVITY ohm-cm.	1.0x10 ¹⁵	1.9x10 ¹⁵	8.4x10 ¹⁵	8.0x10 ¹⁵	4.0x10 ¹⁵	3.4x10 ¹⁵	2.3x10 ¹⁵	not available
DIELECTRIC STRENGTH 0.1in. GAP, KV (RMS)	38	40	41	40	46	42	40	not available
DIELECTRIC CONSTANT (1 KHz)	1.76	1.86	1.86	1.86	1.86	1.90	1.98	78
DISSIPATION FACTOR 1 (KHz), Tan δ	<.0003	<.0003	<.0001	<.0001	<.0003	<.0001	<.0001	not available

* Estimated Values

■ Freezing Point

■ Distilled Water

** Not for specifications purposes. See specification section.

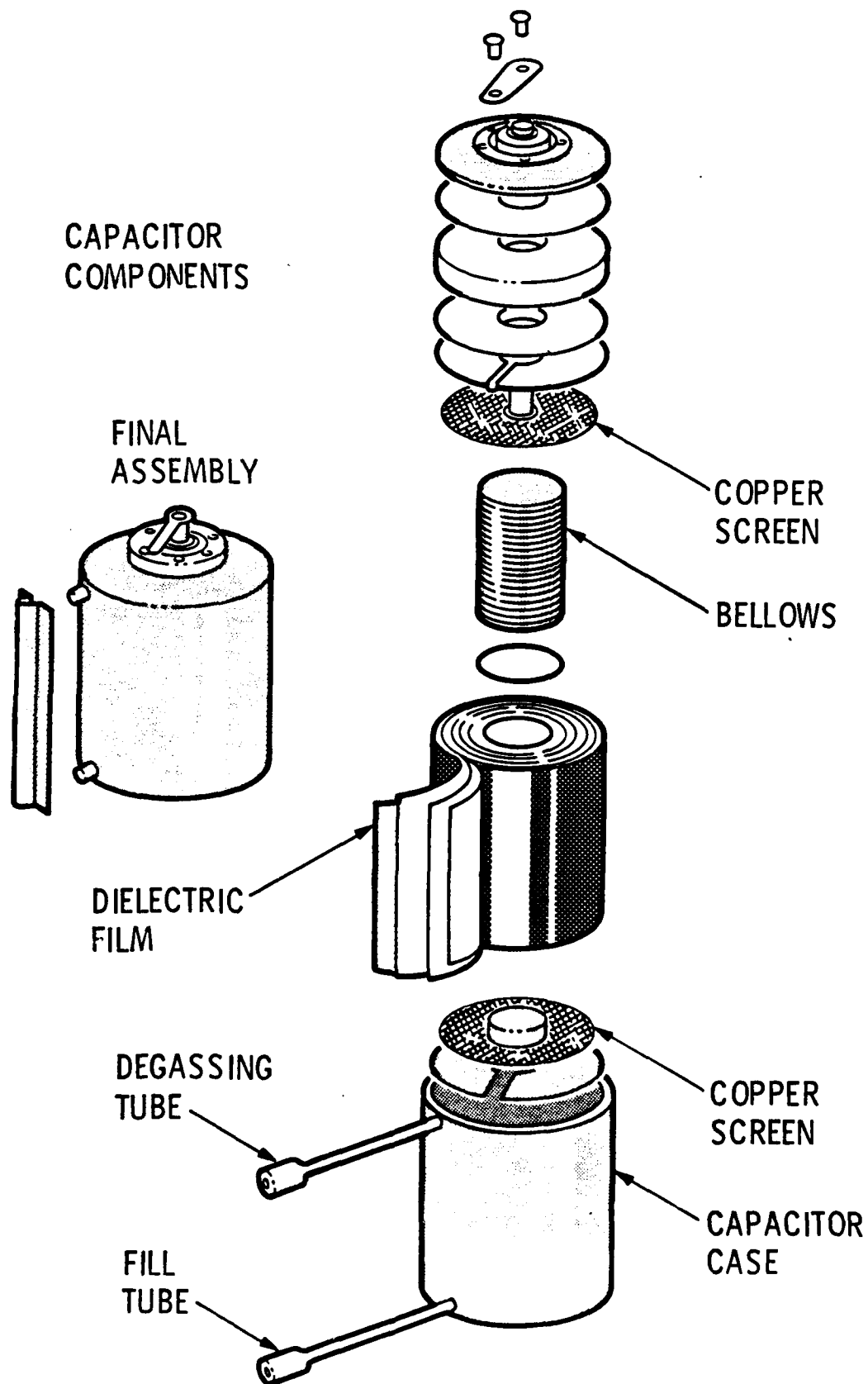
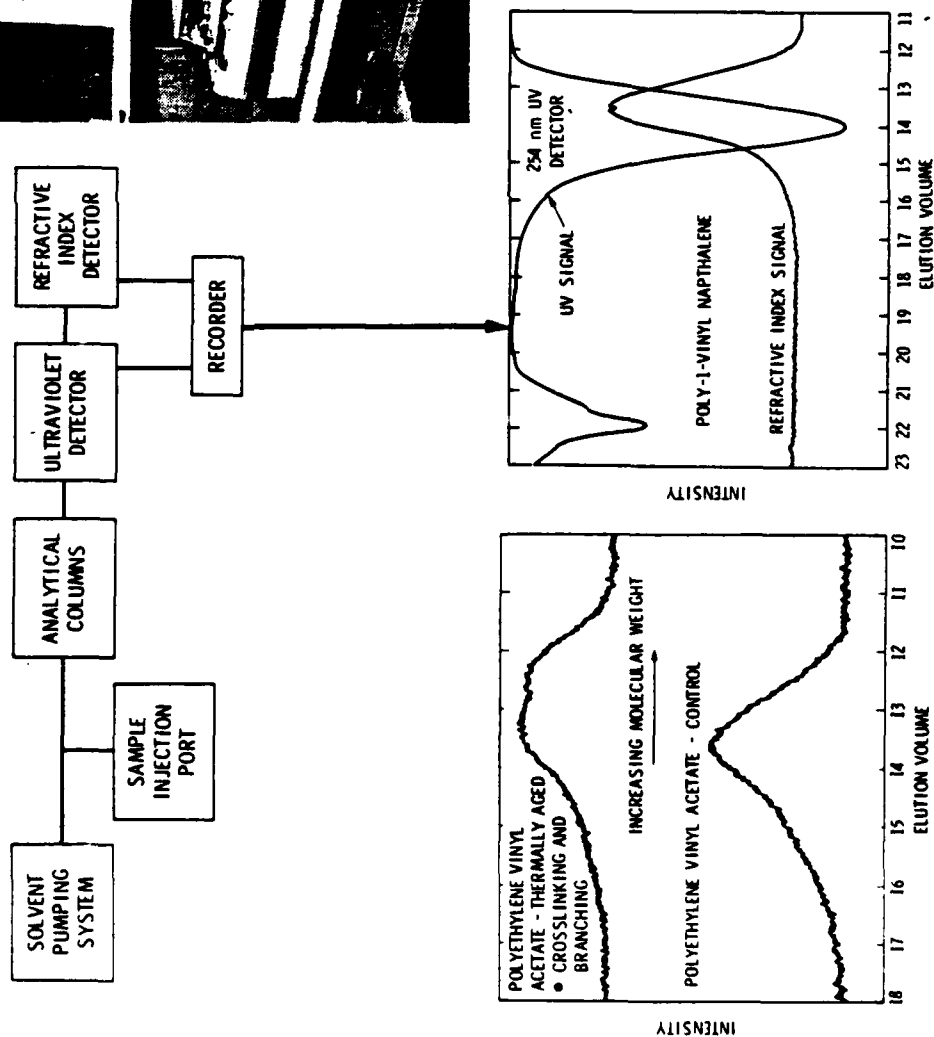
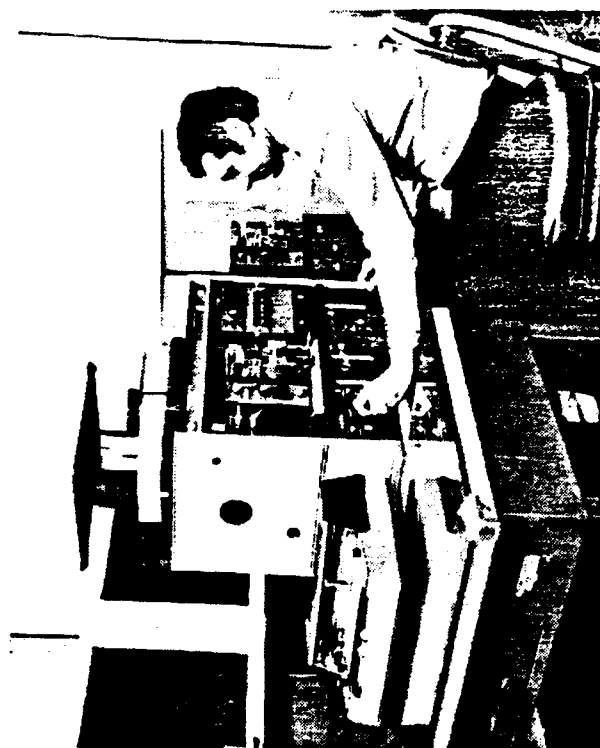


FIGURE 1.

FIGURE 2.

GEL PERMEATION CHROMATOGRAPHY (GPC) FILM (DIELECTRIC) ANALYSIS



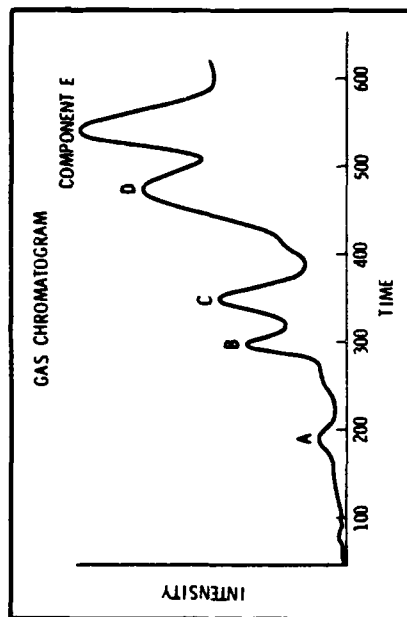
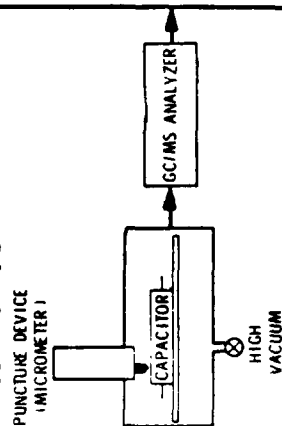
- DETERMINE IMPURITY PRESENCE IN FILM
- MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION
- CORRELATE WITH FILM DEGRADATION

FIGURE 3.

GAS CHROMATOGRAPHY - MASS SPECTROSCOPY (GC/MS)

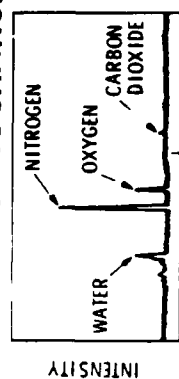
IMPREGNANT ANALYSIS

HIGH VACUUM SAMPLE
CHAMBER ELECTRONIC
PACKAGE-CHEMICAL
ANALYSIS

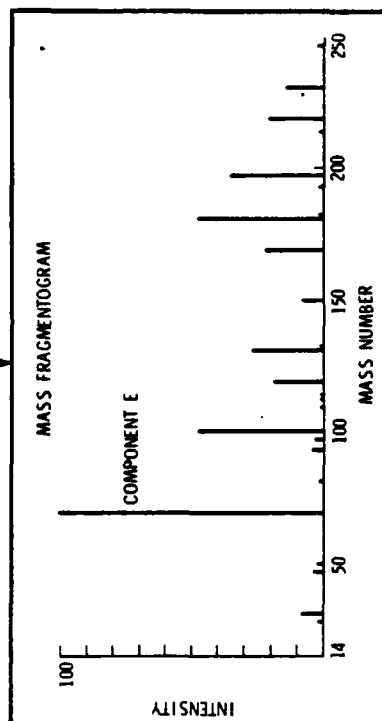
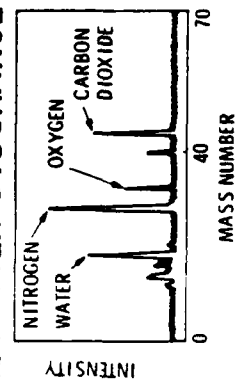


VOLATILE ANALYSIS
OF DRY CAPACITOR/
MASS SPECTRUM

(a) BEFORE DISCHARGE



(b) AFTER DISCHARGE



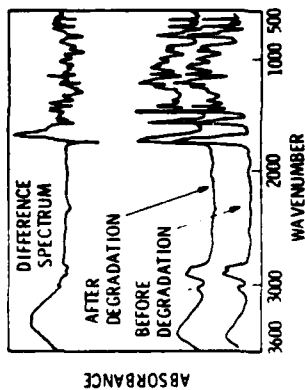
LIBRARY SEARCH
COMPOUND IDENTIFICATION

- DETERMINE PRESENCE AND IDENTITY OF IMPURITY IN IMPREGNANT
- DETERMINE NATURE OF DEGRADATION PRODUCTS/GAS, LIQUID

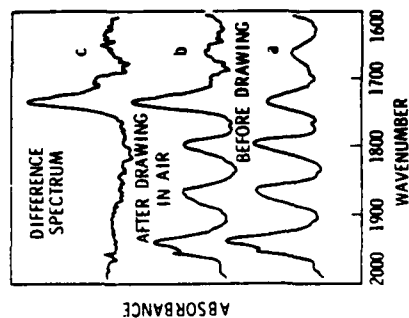
FIGURE 4.

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY FILM (DIELECTRIC) - IMPREGNANT ANALYSIS

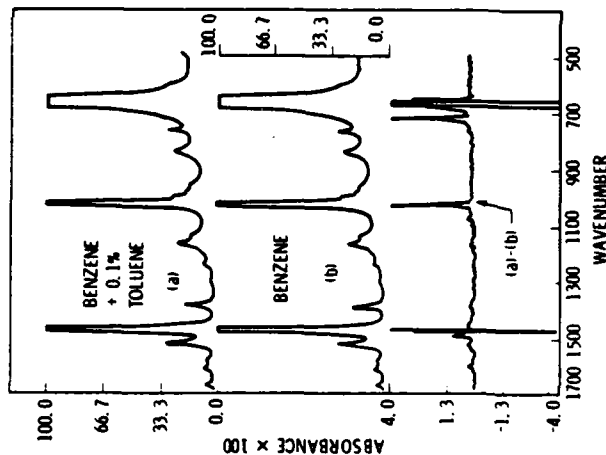
OXIDATIVE DEGRADATION OF CURED EPOXY POLYMER



MECHANICAL DEGRADATION OF POLYSTYRENE IN AIR



DETECTION OF 0.1% TOLUENE IN A BENZENE SOLUTION



- IDENTIFY CHEMICAL STRUCTURE CHANGE OF FILM AND FLUID
- CORRELATE WITH OTHER PHYSICAL/CHEMICAL TESTS
- IDENTIFY NATURE OF CHEMICAL DEGRADATION

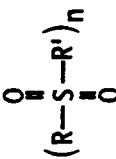
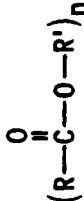
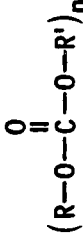
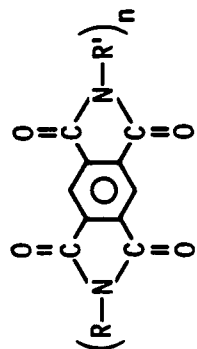
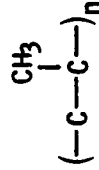
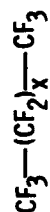
<u>POLYMER</u>	<u>FORMULA</u>	<u>T_g</u> (°C)	<u>T_m</u> (°C)	<u>κ</u>
1) POLYSULFONE		~190°C	—	3.1
2) MYLAR		69°C	~265°C	2.5
3) POLYCARBONATE		158°C -165	232°C -240	2.7
4) KAPTON (POLYAROMATIC IMIDE)				3.6
5) POLYPROPYLENE			167°C	2.5
6) FLUORINERT		<u>b_p</u> 56°C 155°C	1.76 1.86	x = 4 FC-72 x = 10 FC-40

FIGURE 5. Chemical Structure, Glass Transition and Melting Temperatures, and Dielectric Constants of Polymers

FIGURE 6. Chemical(HPLC) and Thermal(DSC) Characterization of Polysulfone and Polycarbonate

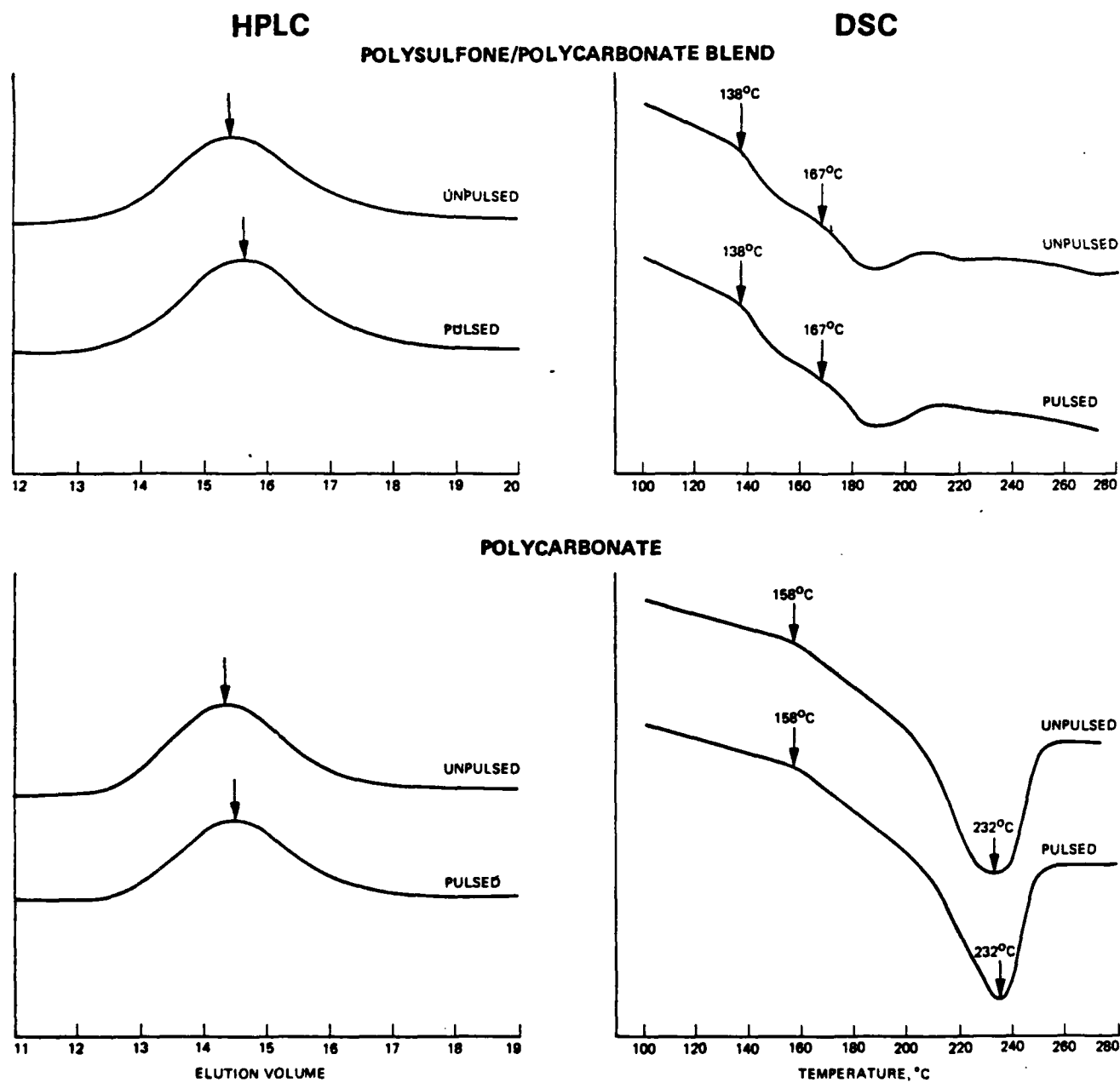
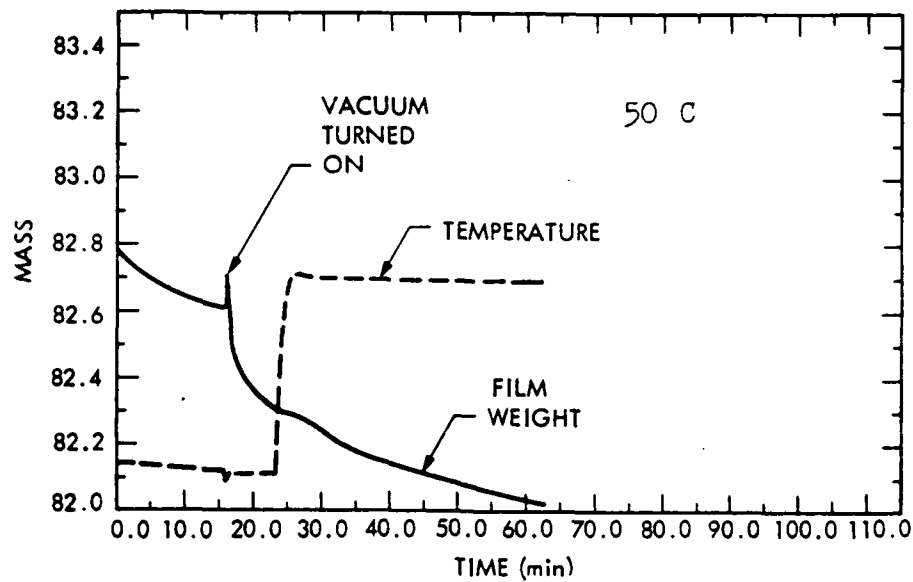


FIGURE 7. Isothermal TGA Measurements of Kapton Film



— TEMPERATURE - TIME PROFILE
- - - FILM MASS - TIME PROFILE

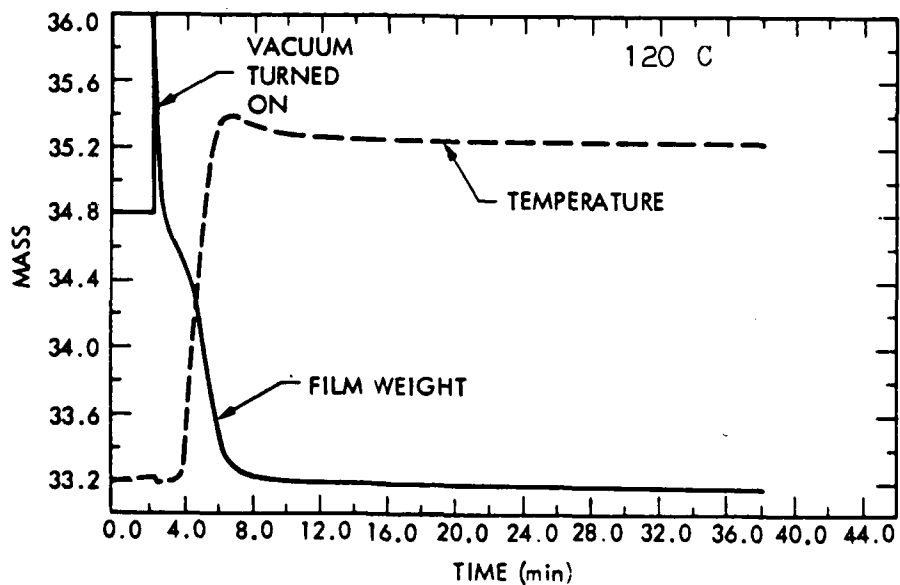


FIGURE 8. FTIR and "Difference" Spectra of Virgin and Pulsed Kapton

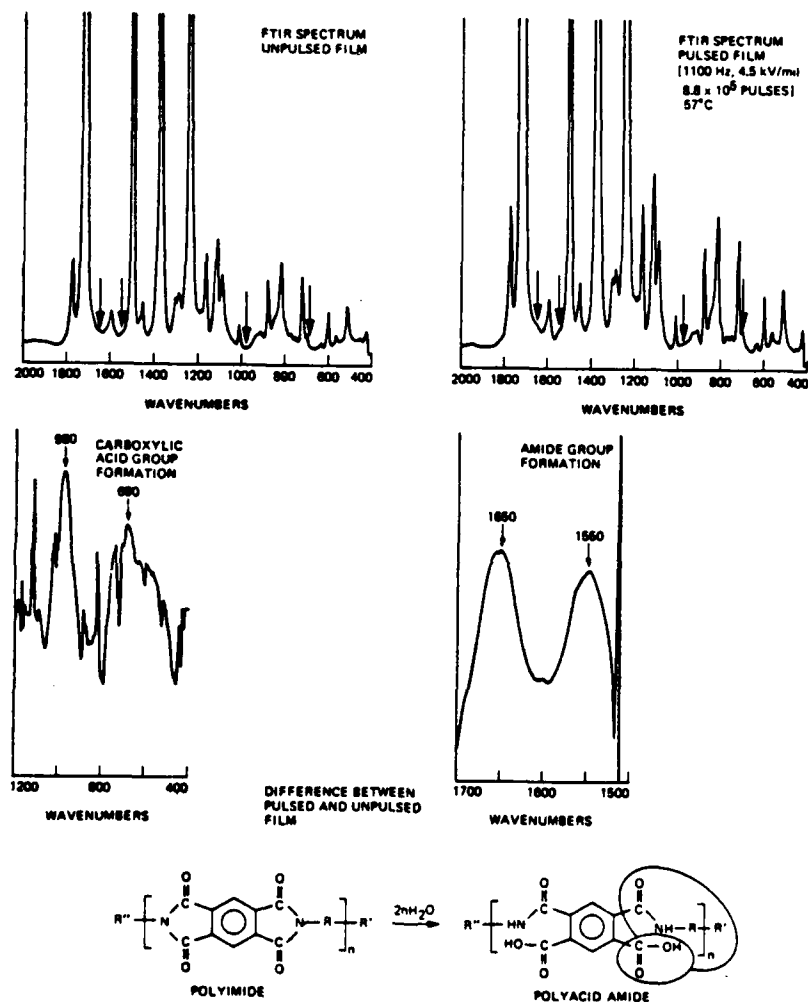
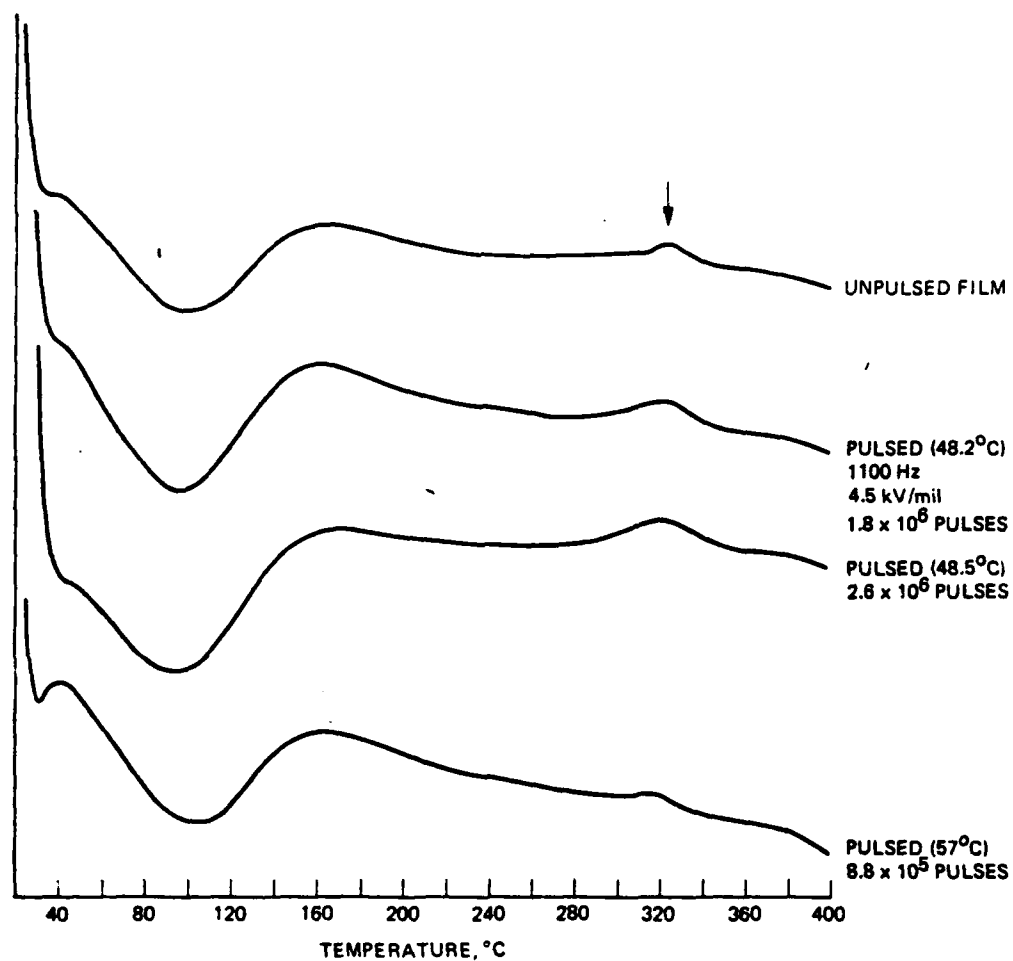
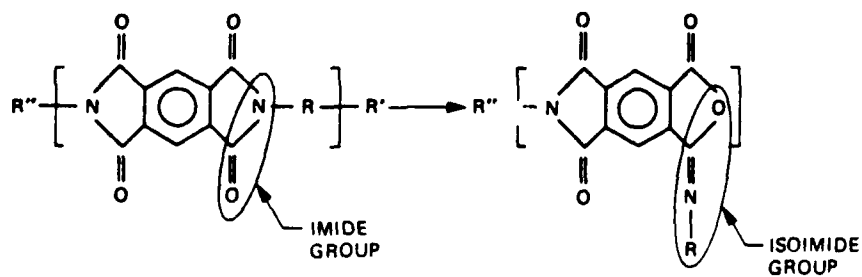


FIGURE 9. DSC Measurements of Virgin and Pulsed Kapton



ISOMERIZATION REACTION AT 320°C:



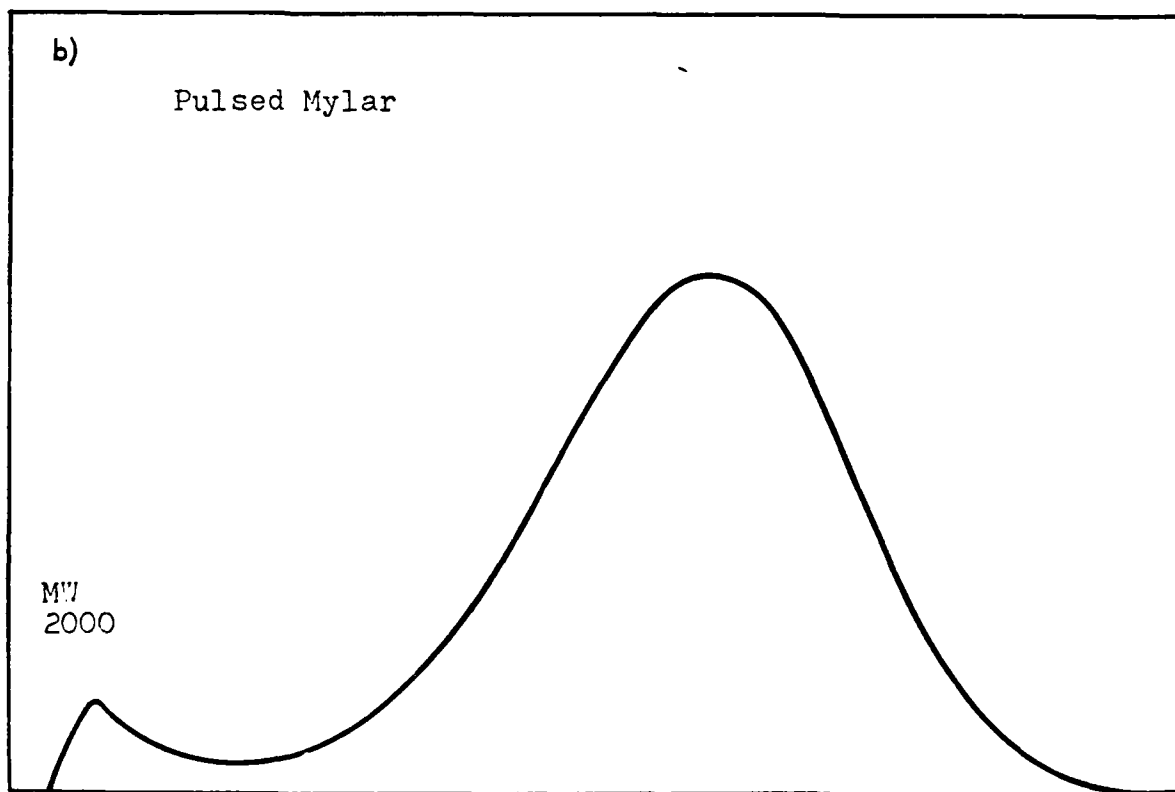
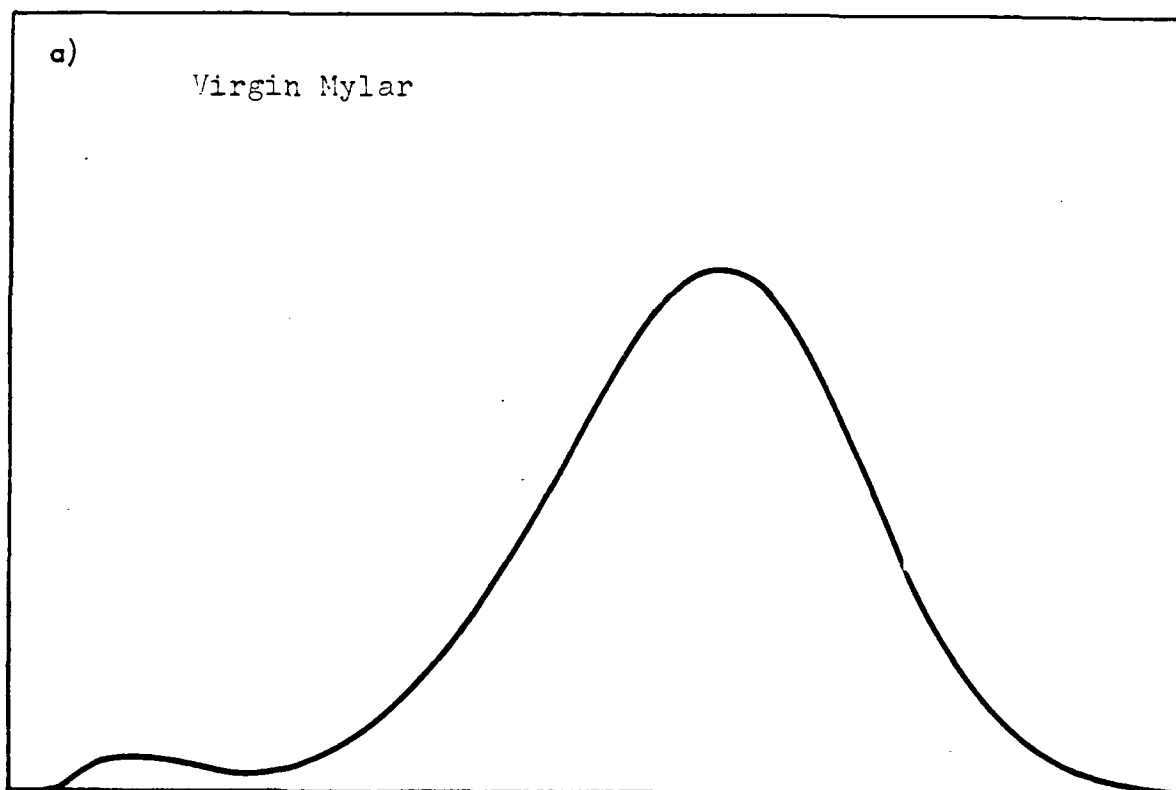
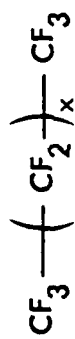
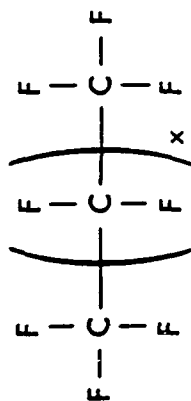


FIGURE 10. Molecular Weight Distribution of Mylar

FIGURE 11. Chemical Structure

FLUORINERT FLUIDS (PERFLUOROCARBONS)



$\underline{\text{X}}$	<u>MOLECULAR WT.</u>
1	188
2	238
3	288
4	338 (FC-72)
10	638 (FC-40)

FIGURE 12. GC/MS Data

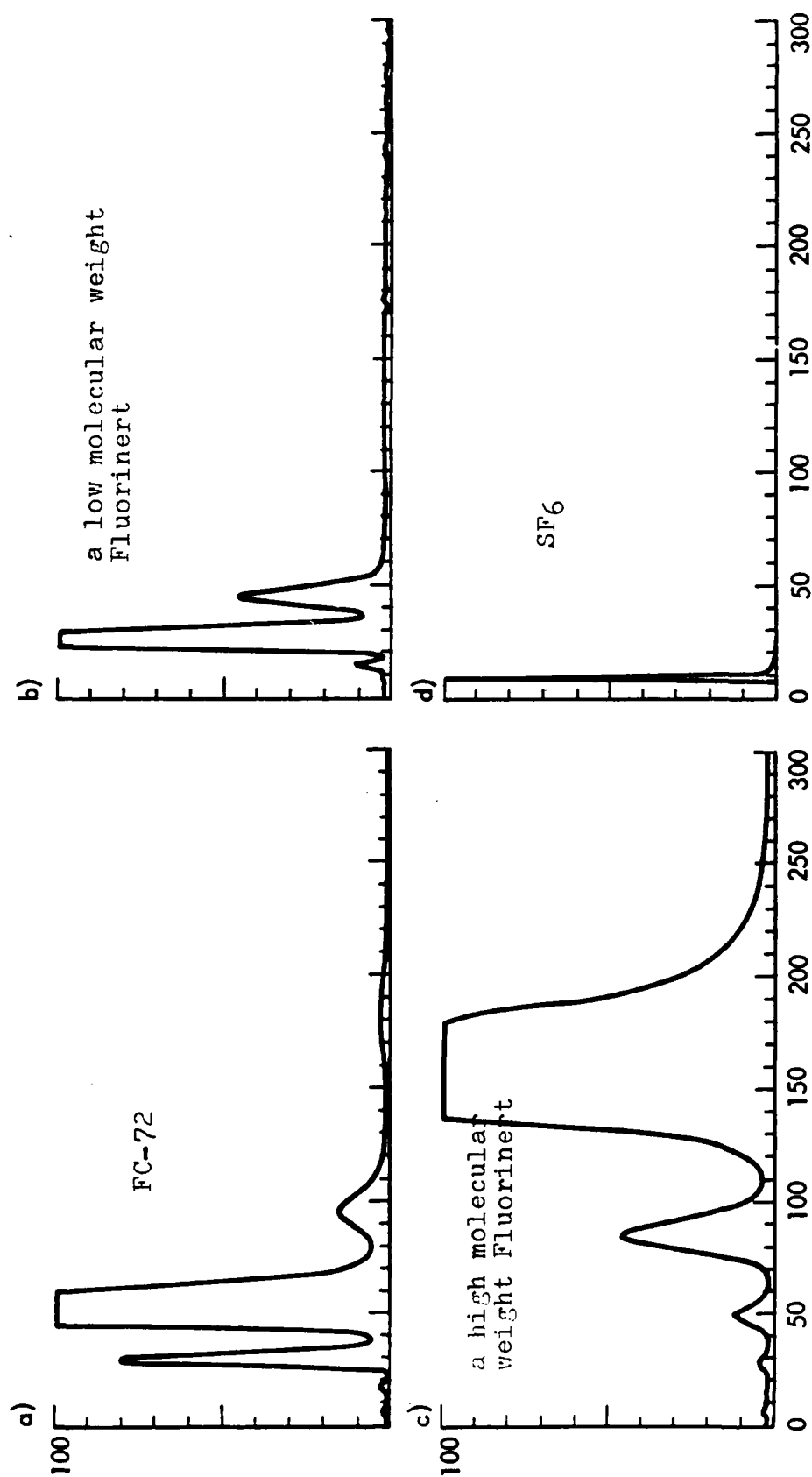
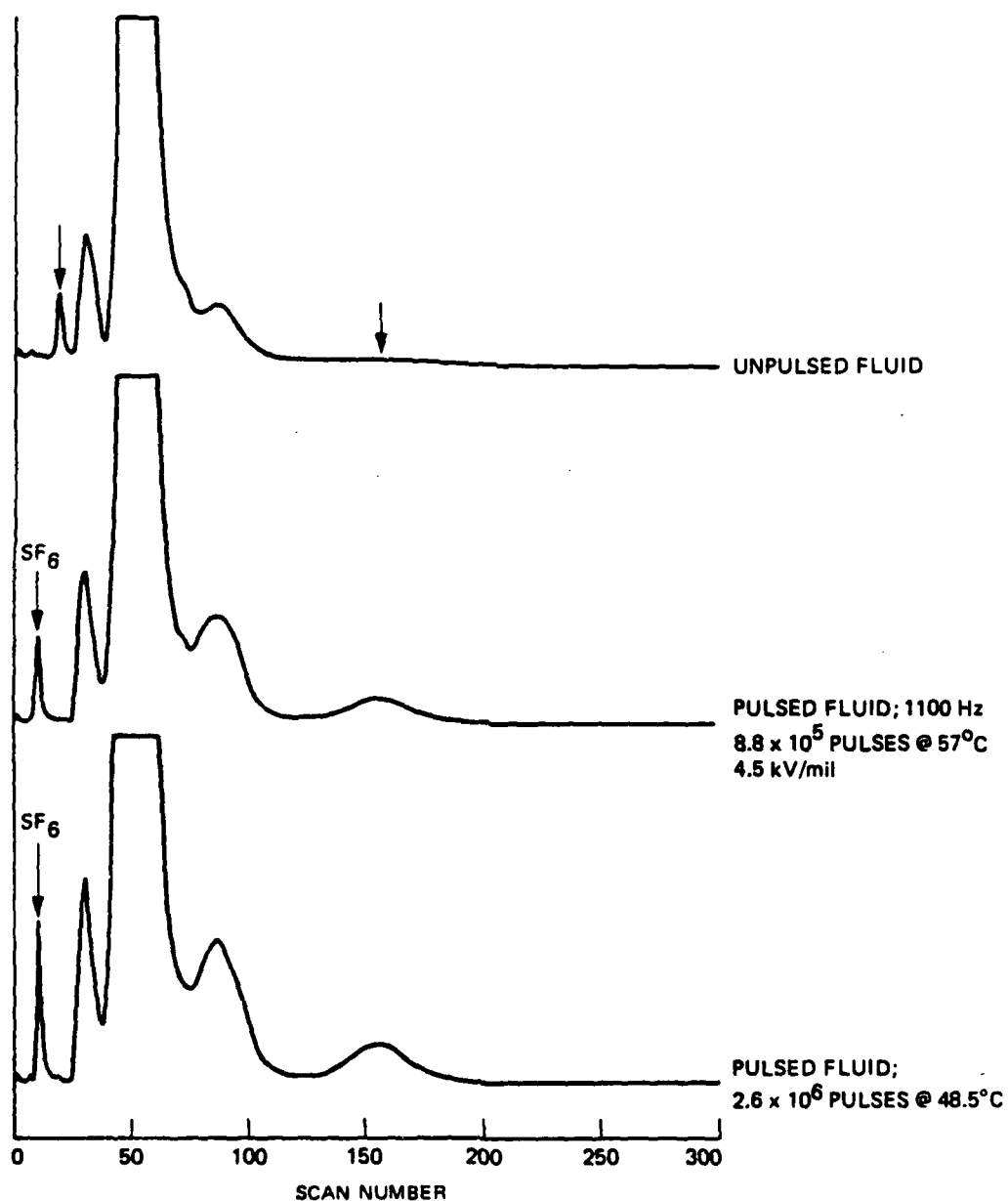


FIGURE 13. GC/MS Data on Pulsed FC-72



APPENDIX

JET PROPULSION LABORATORY

INTEROFFICE MEMO
AC-345-84-099/RH:ba

October 29, 1984

TO: R. Somoano and E. Yen
FROM: R. Haack, Analytical Chemistry Group
SUBJECT: Perfluorocarbon Capacitor Analysis - Test Design and Feasibility.

Evaluation of capacitor performance and interpretation of such results required a type of chemical analysis which could establish the nature of the constituents in the capacitor. The degree of quality control during the manufacturing process and any changes thereafter could be of significance in predicting and understanding the reliability of the capacitor. Although the task is related to previous JPL gas analysis of integrated circuit packages (hermetically-sealed), the capacitors contain primarily a fluid and polymeric film instead of a chip and inert gas. In order to preserve the sample volatile constituents for analysis, the capacitor must be initially analyzed in a vacuum via the mass spectrometer. Other techniques such as GC, GC/MS, FT-IR, and HPLC can be used in later stages of the analysis.

The high vacuum all-stainless steel sample chamber (Figure 1) consists of Varian conflat flanges, thermocouple feed-thru for internal temperature measurements, and a rotary-drive puncture device. A variable-height platform and sample jig in the chamber provides for considerable variation in size of different types of "large" capacitors which might be analyzed. Interfacing of the sample chamber to the mass spectrometer consisted of a batch inlet manifold, gauges, and a variable leak valve (Figure 2).

Four capacitors (2 1/2" x 1 3/4" OD, Sandia National Laboratory) were used for initial testing and method development. The wall thickness (0.035") of the capacitor was decreased in a 1/8" diameter area so that a puncture could be easily made. Three Type J thermocouples mounted on SS washers were attached near the mid-section of the chamber, at the sample platform, and at the bottom of the capacitor case. The sample capacitor, platform, and chamber were cleaned with acetone and then methanol. The assembled unit was then vacuum outgassed at ambient temperature for a minimum of 20 hours before the analysis. Surfaces not in immediate contact with the sample and connecting lines were warmed with a heat-gun in order to increase the clean-up of the system. Prior to puncture of the capacitor, the background of the system was established by using the mass spectrometer.

Technical information supplied by Sandia were as follows:

Dielectric pad: Lexan, number of layers (3, 4, or 5)
Impregnant: FC-72 "Fluorinert" and SF₆
Internal pressure: 47 psia nominal
Operational Data: number of charge/discharge cycles

The manufacturer's data bulletin for FC-72 includes the following characteristics:

<u>Vapor Pressure</u> <u>@ 25°C</u>	<u>Freezing Point</u>	<u>Average</u> <u>mw</u>	<u>Solubility</u>
232 Torr	approx. -100°C	340	48ml air/100ml liquid; 10 ppm H ₂ O (wt)

Mass Spectrometer Analysis

In order to detect the presence of air constituents, trace contaminants, and SF₆ in the presence of the high vapor pressure of FC-72, the sample temperature must be decreased to the point at which there is little vapor pressure contribution by the primary constituent, FC-72. This condition facilitates the sampling of trace levels of argon, oxygen, etc., thru the variable leak valve by the mass spectrometer.

The capacitor was punctured at ambient temperature for two reasons: The contained liquid and gases can readily expand thru the puncture-hole into the sample chamber; secondly, the "burst pressure" can be used as an indication of quality control for a particular type and lot of capacitors.

A typical spectrum (background subtracted) @ 22.1°C is shown in Table I and the corresponding line spectra in Figure 3. Fluorinert liquids typically exhibit major peaks @ M/Z 69 (base peak) 31, 100, 119, and 131. The base peak for SF₆ (mw 146) is M/Z 127. Fortunately, this peak does not contain contribution from FC-72 and therefore could be used in quantitative measurements if a suitable standard mixture is available.

When the temperature of the sample chamber and contents is progressively decreased from ambient, the mass spectra correspondingly exhibits more of the SF₆ contribution and less of that due to the FC-72 ionization pattern. At very low temperatures (near -100°C), the vapor pressure of FC-72 and SF₆ becomes negligible and the spectrum will indicate mainly oxygen, nitrogen, and argon. The freezing point for SF₆ is -50.5°C (CRC Handbook of Chemistry and Physics).

The first capacitor tested (S/N-024) was used to develop a possible analytical procedure. It was determined from mass spectra variation in SF₆/FC-72 contributions that a low temperature would be required and that internal measurement with thermocouples would be necessary. Both the high thermal mass of the stainless steel sample chamber and the decrease of pressure with lowering of temperature result in a slow cooling process (~ 2 1/2 hours) even with the liquid nitrogen dewar.

Conditions, technique, and data accumulation were uniformly maintained for the three capacitors, the results of which are listed in Table II. The burst pressures were not significantly different. If these parts were of the same lot, one might expect less variation in pressure. It is apparent that capacitor (S/N-008) is very different in its relative composition of nitrogen, oxygen, and argon. The value of this data to quality control is that the Sandia representative did inform that argon purging was used at one step in the assembly process. It was also noted that this capacitor was leaking a small amount of FC-72 before puncture. This is apparent from the background spectrum scan of the system. Therefore, the effectiveness of certain steps in the process can later be ascertained as in this case.

The concentration of SF_6 in the capacitor is not closely controlled or known. At the time of puncture of the capacitor at ambient temperature, one can easily identify the presence of SF_6 in the mass spectrum (Table I). The most abundant peak (base peak) for SF_6 appears at M/Z 127. It would be possible to quantitate the SF_6 with a standard having a known $\text{SF}_6/\text{FC-72}$ composition.

CONCLUSION AND RECOMMENDATION:

The sample chamber and method of analysis can be used to identify several data points which may be relative to electrical reliability of the capacitor. After this analysis, the liquid may be removed for other types of analyses.

Continuation of this capacitor reliability study would be enhanced by the following:

1. Availability of samples of FC-72 and SF_6 as used in the manufacturing process. Preparation of standard to be used in quantitation of the ambient mass spectral data.
2. Solubility data for $\text{SF}_6/\text{FC-72}$. Presently, General Electric is conducting such a measurement.
3. Hermeticity testing of the capacitor before submittal for puncture analysis. (Protective epoxy coating on pinch-off tubes should be removed).
4. Capacitor weight before analysis and after removal from the chamber. Estimated weight appears to be $\sim 285\text{g}$. This easy measurement would be another indication of quality control.
5. Mass spectral data will be taken after the puncture of the part at ambient temperature and at the low temperature (approx. -100°C).
6. Recovery of released materials from the capacitor for further analysis (e.g. GC, HPLC, FT-IR).
7. Analysis of the capacitor dielectric pad material for any changes in chemical structure.

TABLE A-1. Mass Spectrum @ 22.1°C, M/Z vs. Intensity

TITLE: S/N 532 PC40-008 B4 AMBIENT
 MASS RANGE : 1-100, 101-250, 251-400
 INTEG. TIME: 2.4, 6
 SECONDS PER SCAN : 1
 FILE 01801 22.1°C SCAN 120-90

AMP. : 23648

	0	.00	.00	.00	.00	.00	.00	.00
	7	.00	.00	.00	.00	.00	.00	.00
	14	.00	.00	.00	.00	.27	.00	.00
	21	.00	.00	.00	.00	.00	.00	.00
	28	.27	.00	.00	5.54	.54	.00	.00
	35	.40	.00	.00	.00	.00	.40	.00
	42	.00	.00	.00	.00	.00	.27	.00
	49	.00	1.48	.94	.00	.00	.81	.00
	56	.00	.00	.00	.00	.00	.00	.27
	63	.00	.00	.00	.00	.00	.94	100.00
	70	1.75	.00	.00	.00	.40	.00	.00
	77	.00	.00	.00	.00	.54	.00	.00
	84	.00	.00	.00	.00	.00	3.38	.00
	91	.27	.00	1.89	.00	.00	.00	.27
	98	.00	.00	5.68	.13	.00	.00	.00
	105	.00	.00	.00	1.28	.00	.00	.00
	112	.33	.00	.00	.13	.00	.00	.00
M/Z 127 SF ₆ base peak (M ⁺ -19)	119	18.80	.40	.00	.00	.00	.00	.00
	126	.00	10.01	.13	.47	.00	6.83	.27
	133	.00	.00	.13	.00	.00	.00	.00
	140	.00	.00	.00	.00	.00	.00	.00
	147	.00	.00	.00	.60	.00	.00	.00
	154	.00	.00	.00	.00	.00	.00	.00
	161	.00	.00	.00	.00	.00	.00	.00
	168	.13	6.02	.20	.00	.00	.00	.00
	175	.00	.00	.00	.00	.00	.00	1.01
	182	.00	.00	.00	.00	.00	.00	.00
	189	.00	.00	.00	.00	.00	.00	.00
	196	.00	.00	.00	.00	.00	.00	.00
	203	.00	.00	.00	.00	.00	.00	.00
	210	.00	.00	.00	.00	.00	.00	.00
	217	.00	.00	.54	.00	.00	.00	.00
	224	.00	.00	.00	.00	.00	.00	.00
	231	.47	.00					

M/Z 69
 FC-72 base peak

TABLE A-2. Capacitor Contents Analysis

S/N	Pressure (Torr)	Temperature (°C)	Relative Concentration (%) ^②		
			M/Z 28 (N ₂ , CO)	M/Z 32 (O ₂)	M/Z 40 (Ar)
SC348PC40-010 E4	320	22.5	81.2	7.3	14.2
	0.2	-101			
	>1	-64			
	>1	-28			
SC432PC40-019 B4	300	20.5	90.8	4.0	5.2
	0.3	-102			
	25	-63			
	87	-26			
SC532PC40-008 B4	369	22.8	22.0	2.3	75.7
	~ 1	-100			
	46	-63			
	122	-30			
SC348PS40-024	235	23	Trial analysis		

① Temperatures below ambient are those measured by TC#2 (platform). For the lowest and intermediate temperatures, the capacitor case was approximately -55°C. A cryopump effect @ low temperatures would concentrate the FC-72 and SF₆ liquids at the bottom of the chamber.

② Values are normalized to total intensity sum and do not include the use of sensitivity factors for this particular instrument. The same analytical procedure for accumulating data was used for the three capacitors.

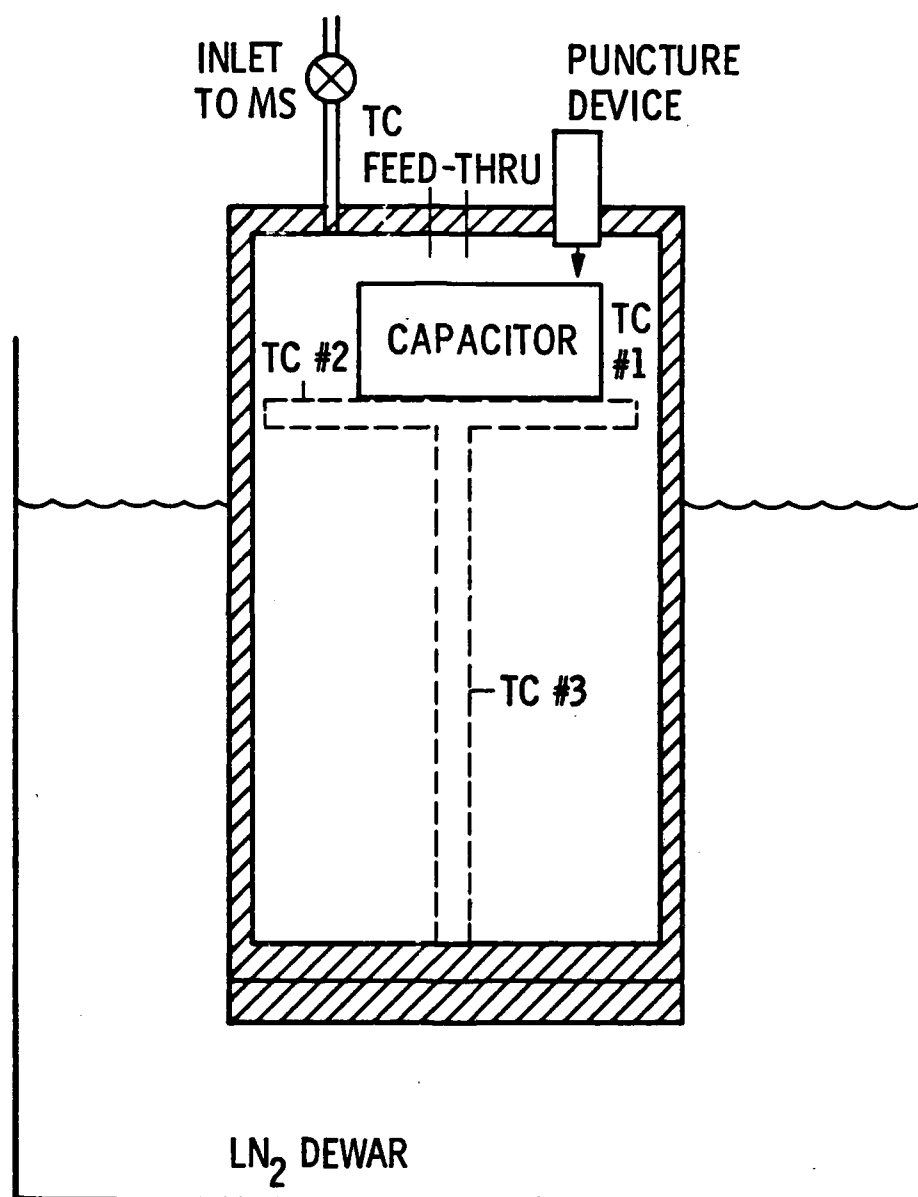


Figure A-1.

Figure A-2.
The Insitu
Capacitor Gas
Analysis Cell

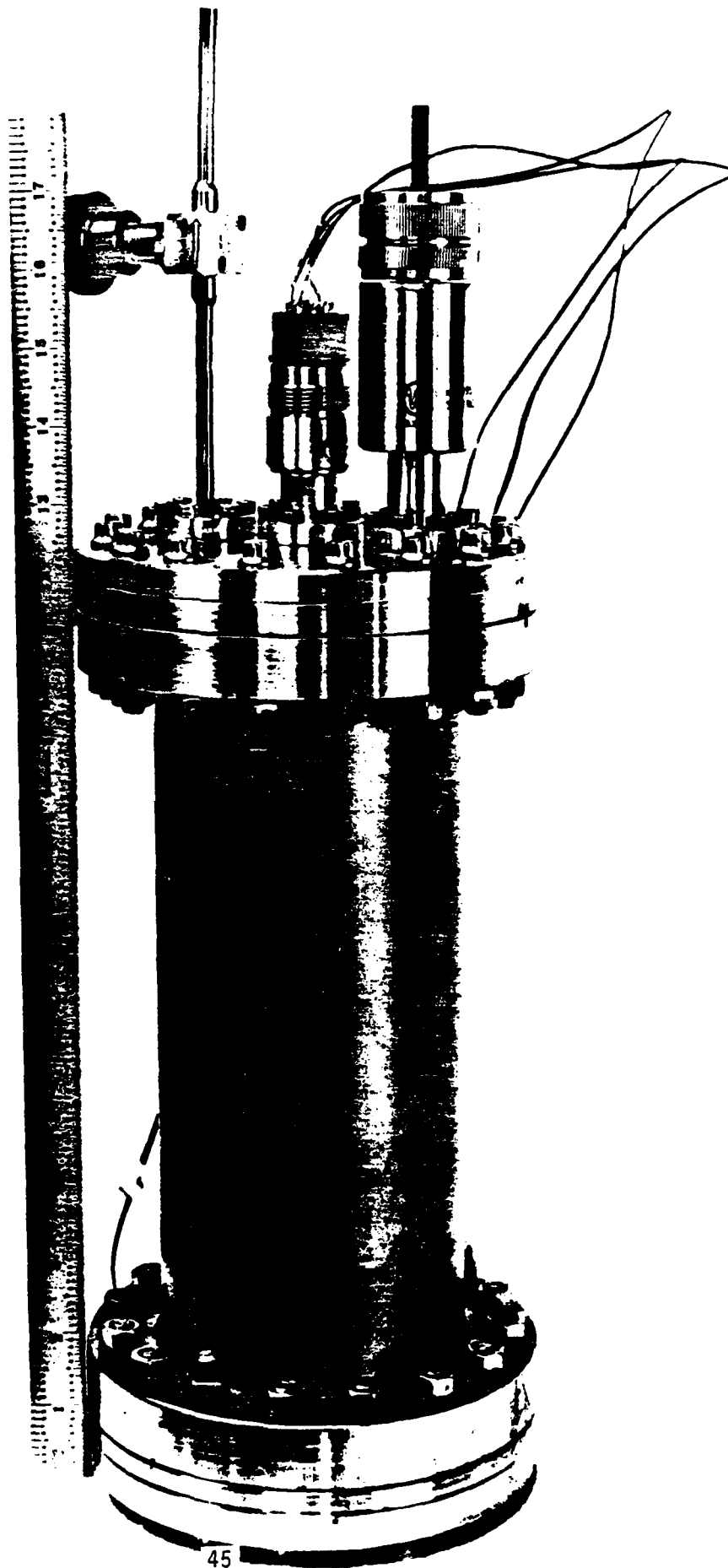
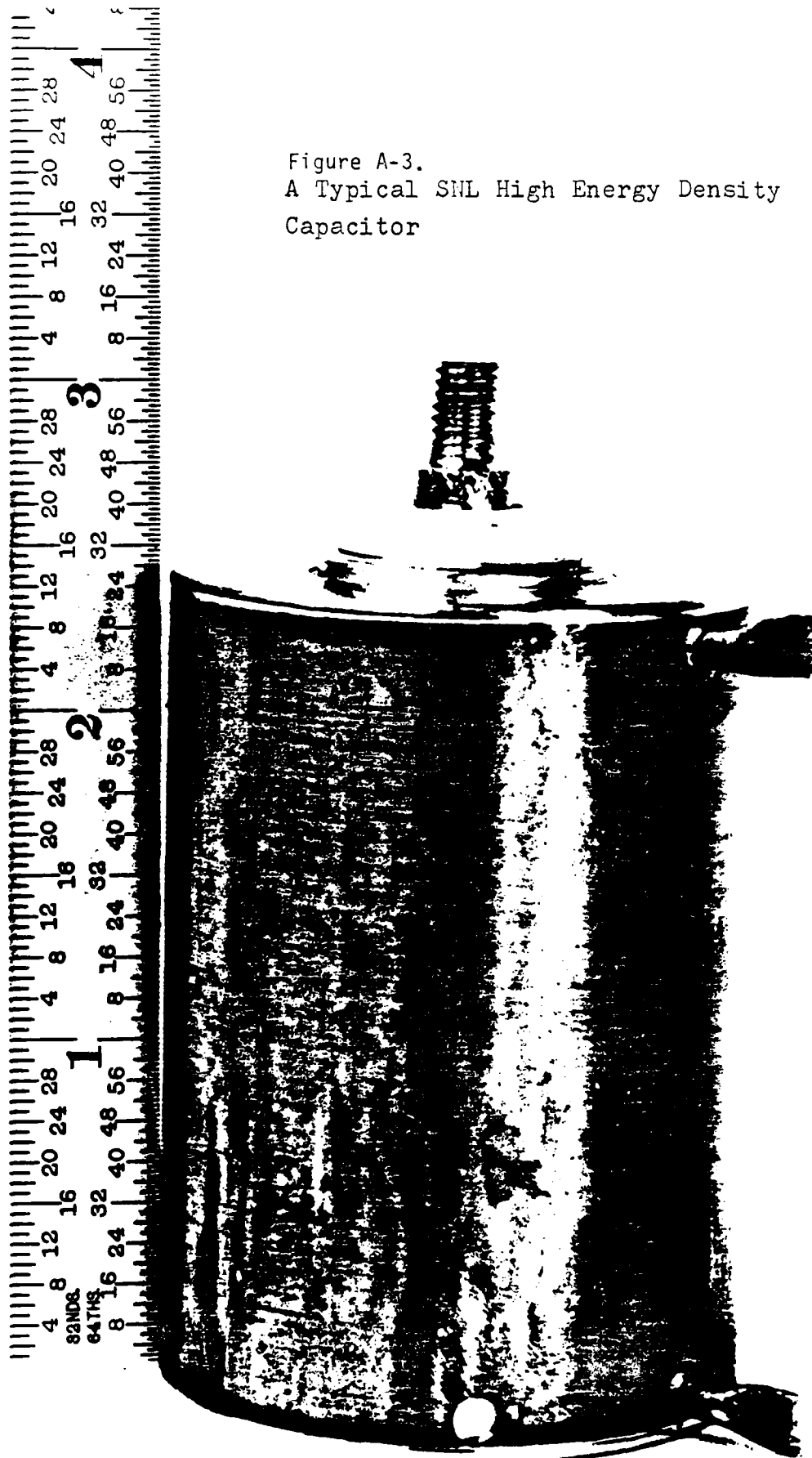


Figure A-3.
A Typical SNL High Energy Density
Capacitor



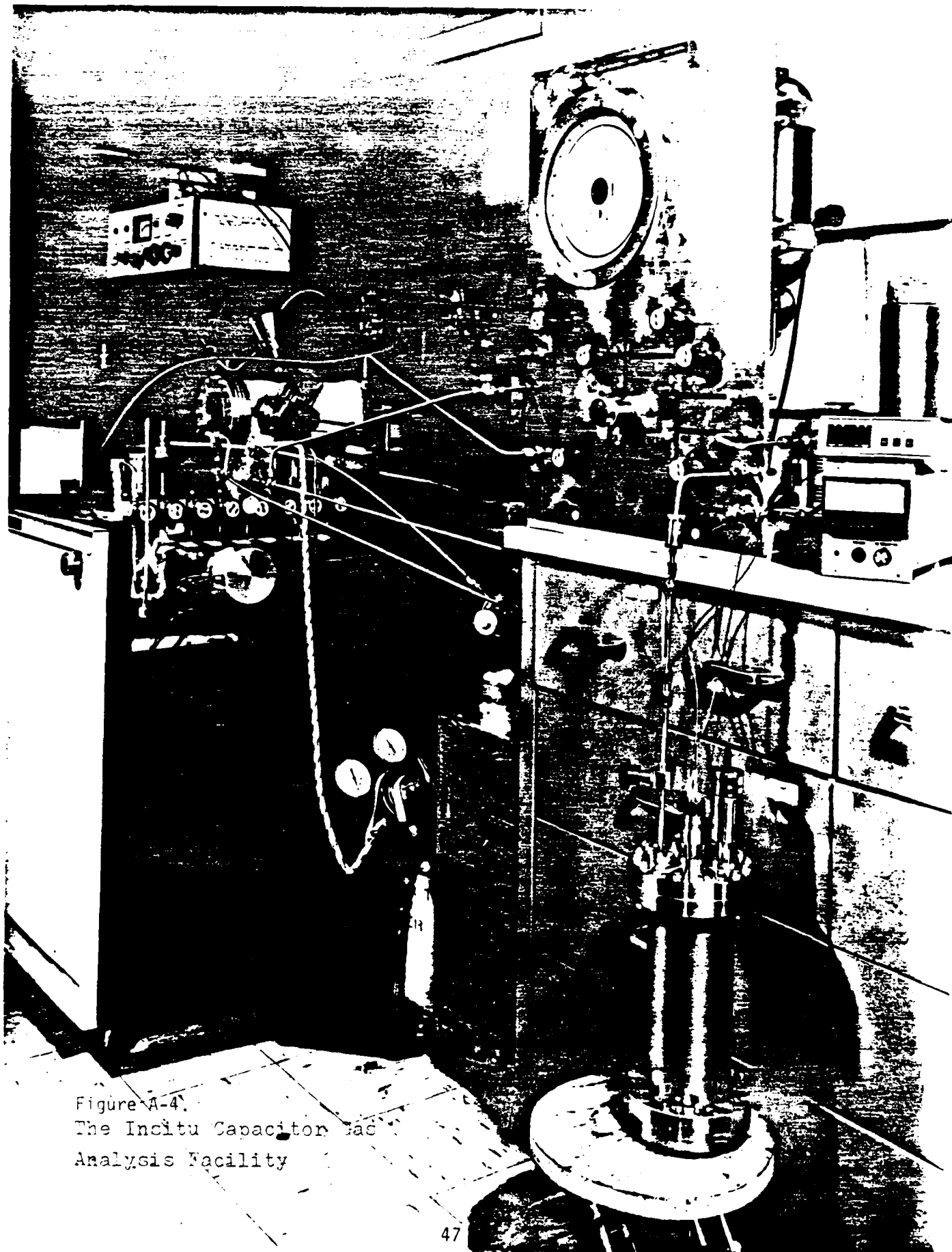


Figure A-4.
The Incitu Capacitor Gas
Analysis Facility

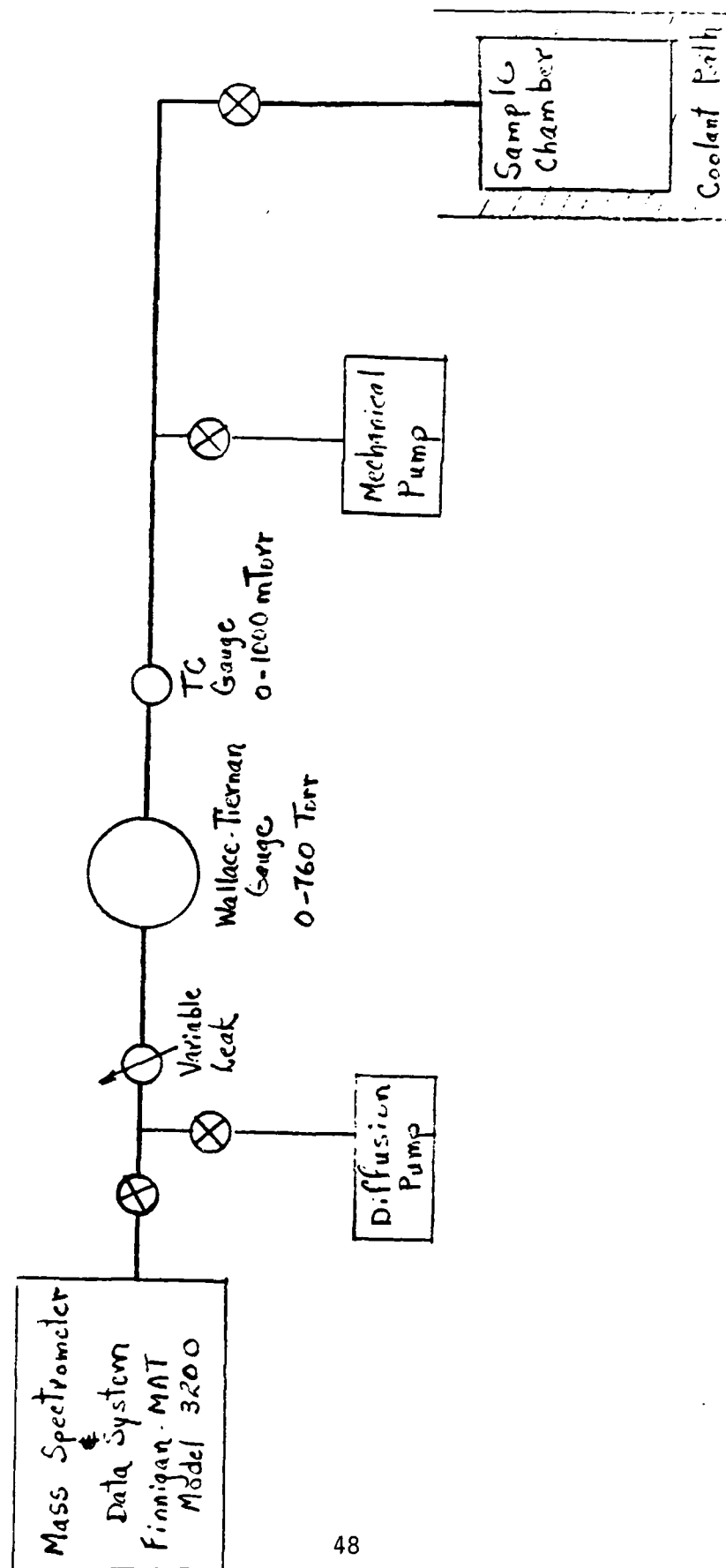


Figure A-5. Equipment Schematic

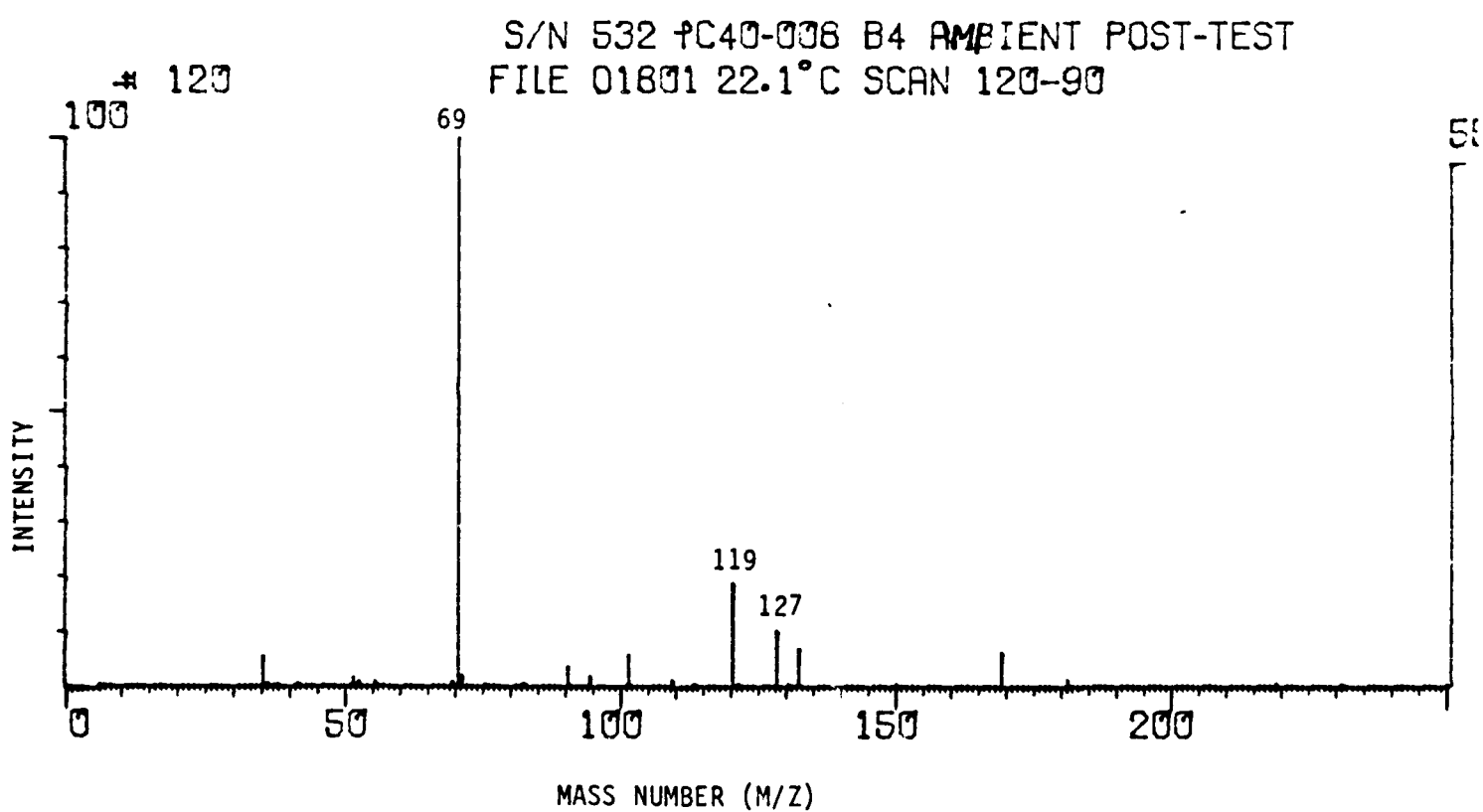


Figure A-6. Mass Spectrum @ 22.1°C